Chem. Pharm. Bull.
36(10)3816—3825(1988)

Synthesis and Reactions of 1-Thianaphthalenes

MIKIO HORI,* TADASHI KATAOKA, HIROSHI SHIMIZU,
and HARUMI AOKI

Gifu Pharmaceutical University, 6–1, Mitahora-higashi 5-chome,
Gifu 502, Japan

(Received March 8, 1988)

Treatment of 1-methyl-4-phenyl-1-thio-2*H*-chromenium perchlorate (**2**) with sodium hydride yielded a dimeric compound **4** and two rearrangement products **5** and **6** *via* unstable 1-methyl-4-phenyl-1-thianaphthalene (**3**). On heating with potassium hydroxide in ethanol, 1-methyl-2,4-diphenyl-1-thio-2*H*-chromenium perchlorate (**9**) gave a dimeric compound **13** and two ring-opened products **11a** and **12a**, but no rearrangement product. On the other hand, 2-cyano-1-methyl-4-phenyl-1-thianaphthalene (**20**) prepared from the corresponding 1-thiochromenium salt **19** by treatment with triethylamine in ethanol was quite stable, and it is the first example of a stable and crystalline 1-thianaphthalene.

Reactions of the 1-thianaphthalene **20** with electrophiles such as tetracyanoethylene, maleic anhydride, and 4-phenyl-1-thianaphthylium perchlorate gave the dimeric compound **23**. However, the treatment of **20** with dimethyl acetylenedicarboxylate yielded a new ring expansion product **27** having a sulfur-containing nine-membered ring.

Keywords——thiabenzene; cyclic sulfur ylide; 1-thianaphthalene; ring expansion; 1,2-rearrangement; 1,4-rearrangement; dimerization; electrophile

In our continuing studies on the chemistry of cyclic sulfur ylides "thiabenzenes," in which the ylide bond forms part of a cyclic conjugated ring system containing six π-electrons, we have already reported the synthesis and reactivities of 2-thianaphthalenes,[1] 9-thiaanthracenes,[2] and 9-thiaphenanthrenes.[3] This paper describes the generation of unstable 1-thianaphthalenes and the first synthesis and some reactivities of stable 1-thianaphthalenes.[4]

Results and Discussion

Synthetic Approach to the 1-Thianaphthalenes

In 1974, Hortmann *et al.* reported that attempts to prepare 1-thianaphthalenes from the reaction of the corresponding 1-thio-2*H*-chromenium salts with base had been unsuccessful, giving a complex mixture of unidentified products.[5] In the course of our studies on thiabenzenes, we have also continued to synthesize 1-thianaphthalenes and succeeded in the generation of the unstable 1-thianaphthalenes as intermediates.

Treatment of 4-phenyl-1-thio-2*H*-chromene[6] (**1**) with methyl iodide in the presence of silver perchlorate in 1,2-dichloroethane afforded 1-methyl-4-phenyl-1-thio-2*H*-chromenium perchlorate (**2**) in 89% yield. The perchlorate **2** was allowed to react with sodium hydride in anhydrous tetrahydrofuran (THF) under nitrogen to afford crystalline and oily products in 16 and 23% yields, respectively, after separation by silica gel preparative thin layer chromatography (PLC). The crystalline product has the molecular formula $C_{32}H_{28}S_2$ based on microanalysis and mass spectral data showing the molecular ion peak at *m/z* 476. Its proton nuclear magnetic resonance (^{1}H-NMR) spectrum ($CDCl_3$) showed peaks at δ 2.32 (6H, s, SMe), 6.0—6.9 (4H, m, olefinic H), and 7.0—7.5 (8H, m, aromatic H). These data are in good accordance with the structure **4** for the crystalline compound. The stereo-structure of the double bonds

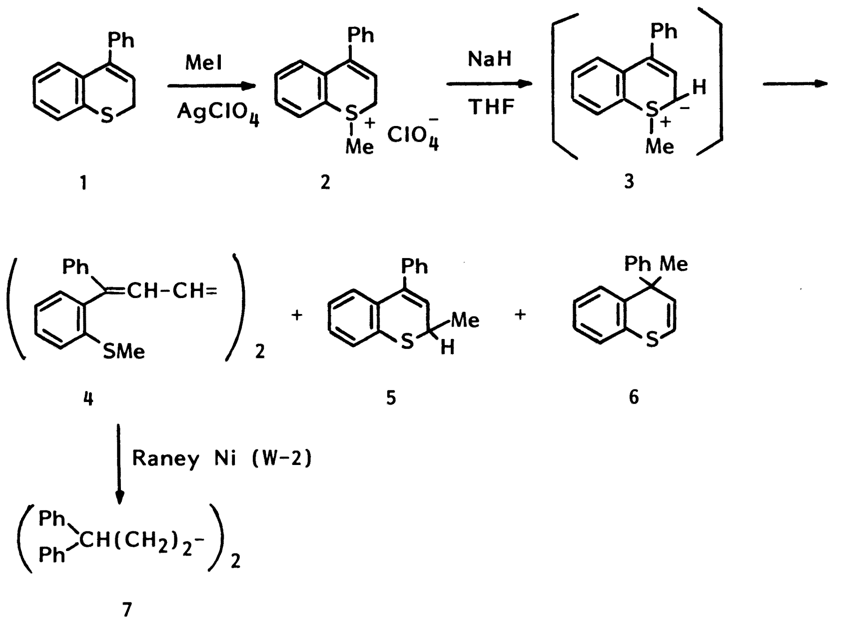


Chart 1

was not determined since the coupling constants were quite complex. The structure of compound **4** was further confirmed by leading **4** to the known compound **7**,7) by desulfurization and hydrogenesis with Raney nickel (W-2). The oily compound obtained above was an inseparable mixture of two isomers **5** and **6**, whose structures were established by their microanalytical and ^{1}H-NMR spectral data. The ^{1}H-NMR data showing a methyl signal at δ 1.45 as a doublet ($J = 7.5$ Hz) were assigned to **5**, and those showing a singlet methyl signal at δ 1.75 were assigned to **6**. The product ratio of **5** and **6** was 4 : 1 based on the integrals of the methyl signals in their ^{1}H-NMR spectra.

The following mechanism *via* 1-thianaphthalene **3** as an intermediate is considered reasonably for the formation of the above products (Chart 1). The sulfonium salt **2** initially generates the unstable 1-thianaphthalene **3** on treatment with base, and this immediately decomposes to give the dimeric compound **4**, and undergoes 1,2- and 1,4-methyl migration to afford **5** and **6**, respectively. Concerning the formation of **4**, it is possible that the ylide intermediate **3** first decomposes to a carbene intermediate, which dimerizes to give **4**. However, this seems unlikely based on the following experimental evidence. When the base (ethanolic KOH solution) was added little by little to the suspension of **2** in ethanol, the dimeric product **4** was obtained in higher yield (68.3%) than in the case of reverse addition, that is, under the conditions in which the sulfonium salt **2** and ylide **3** coexist in the reaction medium, the yield of the dimeric compound **4** increased. This result suggests that the formation of **4** was caused by the ionic reaction of **2** and **3** rather than by carbene coupling (Chart 2). An analogous dimerization reaction was reported by Flowers *et al.*8) Next, we attempted the synthesis of 1-methyl-2,4-diphenyl-1-thianaphthalene having two phenyl groups at the 2- and 4-positions which may contribute significantly to the stabilization of the naphthalene by delocalization of the ylide carbanion to the phenyl group (Chart 3). On treatment of 2,4-diphenyl-1-thio-2*H*-chromene (**8**) with methyl iodide in the presence of silver perchlorate in 1,2-dichloroethane, 1-methyl-2,4-diphenyl-1-thio-2*H*-chromenium perchlorate (**9**), mp 161 °C was synthesized in 88% yield as a sole configurational isomer. The configuration is presumed to be the sterically more stable *trans* form. As a by-product, 2,4-

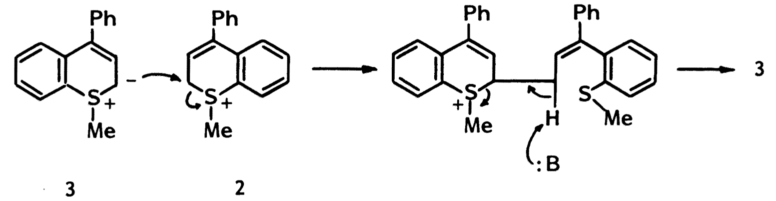


Chart 2

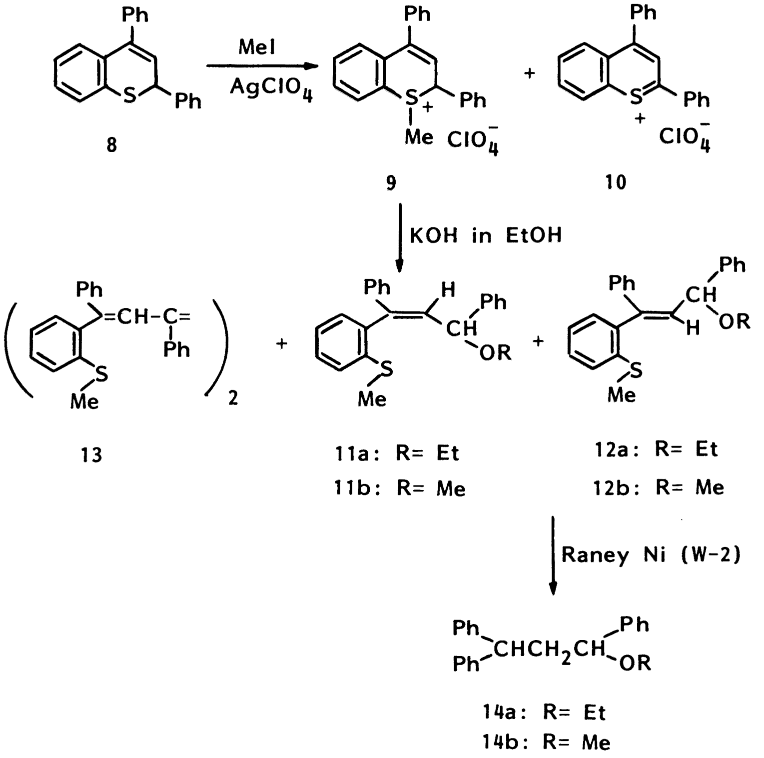


Chart 3

diphenyl-1-thianaphthylium perchlorate (**10**) was obtained in 2% yield. The structure of **10** was established by comparison with an authentic sample.[6] Analogous oxidative aromatization was observed in the reaction of 2,4,6-triphenylthiopyran with methyl iodide, affording 2,4,6-triphenylthiopyrylium iodide.[9]

The reaction of the perchlorate **9** with potassium hydroxide in absolute ethanol under nitrogen gave, after separation by PLC, a 19.8% yield of yellow crystals, mp 210—211 °C and a 25.3% yield of a colorless oil. The structure of the crystalline product was unequivocally established on the basis of the following facts. Microanalytical and mass spectral data confirmed the molecular formula as $C_{44}H_{36}S_2$. The ^{1}H-NMR spectrum ($CDCl_3$) showed an S-methyl signal at δ 2.18 and olefinic and aromatic proton signals at δ 6.71—7.35 as a multiplet. These data are consistent with the structure **13**. The oily product was found to be a mixture (*ca.* 1 : 1) of two isomers from the ^{1}H-NMR spectrum. Their structures were confirmed as **11a** and **12a** on the basis of microanalytical, mass, and ^{1}H-NMR spectral data. These structures were further confirmed by chemical conversion to the propane derivative **14a** as a sole product by desulfurization with Raney nickel (W-2). When treated with sodium hydride in THF the

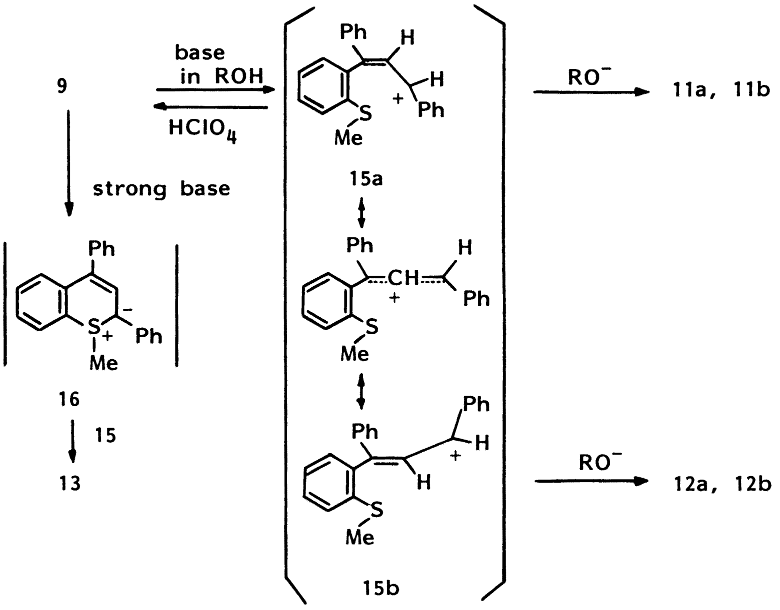


Chart 4

perchlorate **9** gave a 65% yield of **13**.

Next, in order to get more information pertaining to the reaction mechanism, we carried out the following experiments. A solution of **9** in absolute ethanol was stirred for 3 d, but only small amounts of **11a** and **11b** were detected in the ^{1}H-NMR spectrum of the reaction mixture and almost all of the starting material was recovered unchanged. When treated with 2 eq of triethylamine in ethanol, the perchlorate **9** reacted with alcohol to give an 88% yield of **11a** and **11b** as a mixture (0.9 : 1). Moreover, on treatment of **9** with triethylamine in methanol, **12a** and **12b** were obtained in 80% yield as an inseparable mixture (1 : 1). The above ring-opened products **11a**, **11b**, **12a**, and **12b** afforded the perchlorate **9** in high yield on treatment with 70% perchloric acid.

On the basis of all the experimental results mentioned above, the following mechanism for the formation of **11**, **12**, and **13** can be put forward (Chart 4). The perchlorate **9** undergoes ring opening at the S–C$_2$ bond to form a carbocation intermediate **15a** (in a protic solvent) in the presence of base. The intermediate **15a** resonates with another intermediate **15b**. These intermediates are attacked nucleophilically by alcohol (or alkoxide) to give **11** and **12**. However, when strong bases such as potassium hydroxide or sodium hydride are used, the deprotonated species, 1-methyl-2,4-diphenyl-1-thianaphthalene (**16**) is formed in addition to the ring-opened intermediate **15**. 1-Thianaphthalene **16** reacts with the intermediate **15** to give the dimeric compound **13**.

Synthesis of Stable 1-Thianaphthalene

As mentioned above, 2-unsubstituted **3** or 2-phenyl-1-thianaphthalene **16** generated from the corresponding 1-thiochromenium salt **2** or **9** by deprotonation with base was too unstable to be isolated. Now, we succeeded in the isolation of a novel and stable 1-thianaphthalene derivative having a strong electron-withdrawing group (cyano group) at the 2-position, which contributes to the delocalization of ylide carbanion.

Synthesis and Thermal Rearrangement of 2-Cyano-1-methyl-4-phenyl-1-thianaphthalene (20)

The synthesis of **20** was conducted as shown in Chart 5. Treatment of 4-phenyl-1-

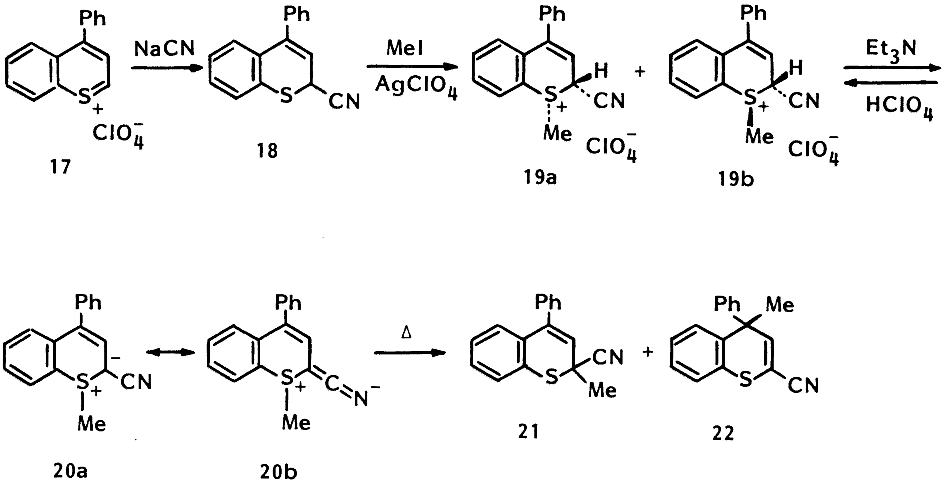


Chart 5

thianaphthylium perchlorate⁶⁾ (**17**) with sodium cyanide in dichloromethane and a small amount of water gave 2-cyano-4-phenyl-1-thio-2*H*-chromene (**18**) in 91% yield. The cyano compound **18** was methylated with methyl iodide in the presence of silver perchlorate to afford 2-cyano-1-methyl-4-phenyl-1-thio-2*H*-chromenium perchlorate (**19**) in 84% yield. The sulfonium salt **19** was obtained as an inseparable mixture of *cis* **19a** and *trans* isomers **19b** (ratio of *cis* and *trans*: 1 : 1.4 in CF_3CO_2H by ^{1}H-NMR). The methyl signal of the *cis* isomer **19a** appeared at lower field (δ 3.54) than that of the *trans* isomer (δ 3.48) due to the anisotropic effect of the cyano group oriented in *cis* configuration. Deprotonation of **19** with triethylamine in ethanol at room temperature yielded 2-cyano-1-methyl-4-phenyl-1-thianaphthalene (**20**) as stable yellow prisms in 98% yield. The thianaphthalene **20** is very soluble in chloroform or dichloromethane, but only slightly soluble in ether. The absorption band of the cyano group in the infrared (IR) spectrum of **20** is stronger and shifts to lower wave number (2170 cm^{-1}) than that of an ordinary cyano group, which indicates delocalization of the carbanion electron of **20** to the cyano group, and suggests that the resonance form **20b** is an important contributor to the electronic distribution in **20**. The ^{1}H-NMR spectrum of **20** showed a singlet signal of 3-H in the olefinic region (δ 6.80) and a methyl signal at δ 2.26. The thianaphthalene **20** was treated with perchloric acid to afford 1-thio-2*H*-chromenium perchlorate **19**. The above spectral and chemical observations reveal the ylidic nature of the 1-thianaphthalene **20**.

The thianaphthalene is very stable at room temperature. However, on heating in acetone for 50 h, **20** decomposed to give 1,2- and 1,4-rearranged products **21** and **22** as an inseparable mixture in 40% yield. The ratio of **21** and **22** was determined as 2 : 1 from the ^{1}H-NMR spectral data. Determination of the structures of **21** and **22** was mainly based on the chemical shifts of H-3 in their ^{1}H-NMR spectra. The H-3 signal of **22** appeared at δ 6.80, while that of **21** appeared at δ 5.82. This difference may be attributed to the fact that H-3 of **22** is more deshielded by the anisotropic effect of the cyano group oriented in the same plane.

Reactions of 2-Cyano-1-methyl-4-phenyl-1-thianaphthalene (20) with Some Electrophiles

It is of great interest to examine the reactivities of the 1-thianaphthalene **20** based on its ylidic nature.

Reaction of the 1-thianaphthalene **20** with the 1-thiochromenium salt **19** in acetone afforded the ring-opened product **23** in 38% yield (Chart 6). The structure of **23** was determined by micro-analysis and from the spectral data.

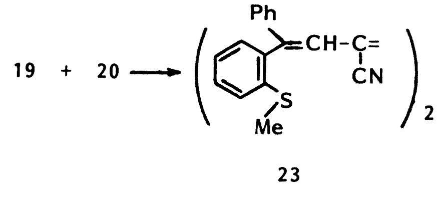
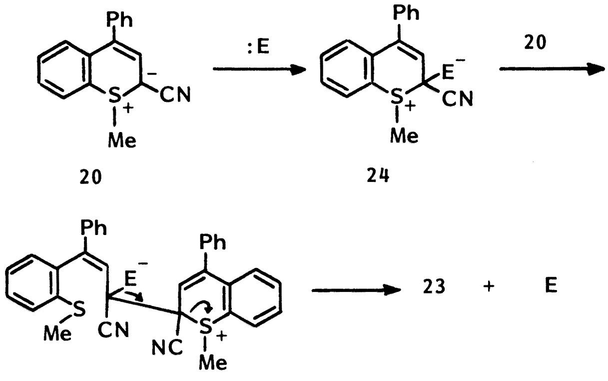


Chart 6



E: TCNE, maleic anhydride, 4-phenyl-1-thianaphthylium perchlorate

Chart 7

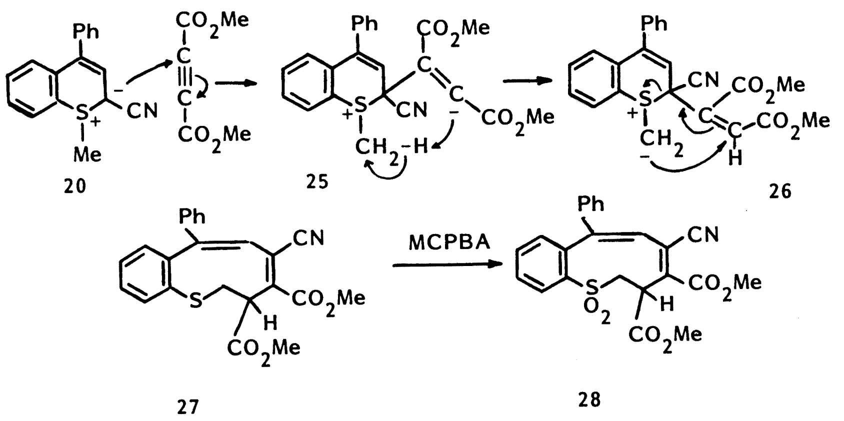


Chart 8

Next, treatment of **20** with tetracyanoethylene (TCNE) in benzene at room temperature also gave **23** in 9.3% yield without any adduct of **20** and TCNE, and some TCNE was recovered. Similarly, **23** was obtained in 10% yield by the reaction of **20** with maleic anhydride in benzene, and also with 4-phenyl-1-thianaphthylium perchlorate (**17**) in 1,2-dichloroethane in 30% yield along with a 77% yield of recovered **17**. In the above reactions, no isolable addition product was obtained. The electrophiles acted as catalysts for the dimeric reactions because electrophiles were recovered in each reaction. Therefore, the mechanism of the dimerization reactions is proposed to be as shown in Chart 7.

We next performed the reaction of **20** with an acetylenic electrophile (Chart 8). Treatment of **20** with 2 eq of dimethyl acetylenedicarboxylate (DMAD) in benzene at room temperature gave an interesting ring expansion product **27** in 12% yield. The structure of **27** was established mainly on the basis of spectral evidence. Elemental analysis and mass spectral data (*m*/*z*, 405 (M^+)) indicate a molecular formula of $C_{23}H_{19}NO_3S$ for the product, corresponding to the 1 : 1 adduct of **20** and DMAD. The IR spectrum showed characteristic absorption bands at 2220 cm^{-1} for the cyano group and at 1740 and 1710 cm^{-1} for the two ester carbonyl groups. The ^{1}H-NMR spectrum showed a characteristic broad doublet signal

($J = 9$ Hz) attributable to C_3-H at δ 4.20, a doublet of doublets signal ($J = 15, 9$ Hz) assignable to one of the methylene protons at δ 2.98, and also a broad doublet signal ($J = 15$ Hz) due to the other methylene proton at δ 3.71. The signal of an olefinic proton at position 6 appeared as a singlet at δ 6.90. The adduct **27** could be led to the corresponding sulfone derivative **28** by oxidation with *m*-chloroperbenzoic acid.

A plausible mechanism for the formation of **27** is depicted in Chart 8. Nucleophilic attack of **20** on the electron-deficient acetylene forms the zwitterionic intermediate **25**, which leads to the sulfonium methylide intermediate **26** by intramolecular proton abstraction from the proximate S-methyl group. Michael-type addition of the carbanion of the ylide intermediate **26** to the olefinic carbon atom, with concomitant fission of S–C_1 bond affords the ring-expanded product **27**.

Concerning the intermediate **24** in Chart 7, when E^- is rather stable as in the cases of TCNE, maleic anhydride, and thianaphthylium salt, the reaction might proceed to give the dimeric product, while when E^- is more basic, as in the case of DMAD, than the above described species, the intramolecular deprotonation might occur to give the sulfonium ylide intermediate **26** in Chart 8.

Experimental

Melting points were determined by using a Yanagimoto micromelting point apparatus and are uncorrected. IR spectra were determined on a JASCO IR A-1 infrared spectrometer. ^{1}H-NMR spectra were run on a Hitachi R-20B spectrometer. Chemical shifts are expressed in parts per million (ppm) with respect to tetramethylsilane as an internal standard. Mass spectra (MS) were obtained with a JEOL D-300 mass spectrometer at an ionization voltage of 70 eV.

1-Methyl-4-phenyl-1-thio-2*H*-chromenium Perchlorate (2)——Silver perchlorate (926 mg, 4.46 mmol) was added portionwise to an ice-cooled solution of 4-phenyl-1-thio-2*H*-chromene[6] (**1**, 1 g, 4.46 mmol) and methyl iodide (6.33 g, 44.6 mmol) in 1,2-dichloroethane (30 ml) with stirring, and the mixture was stirred for 14 h at room temperature. The precipitate was filtered off and washed several times with hot acetone. The filtrate and washings were combined and concentrated *in vacuo* to dryness. The residue was recrystallized from 1,2-dichloroethane–ether to afford 1.34 g (89%) of **2** as pale yellow leaflets, mp 162—164 °C. IR (KBr): 1080 (ClO_4^-) cm^{-1}. ^{1}H-NMR (DMSO-d_6) δ: 3.1 (3H, s, SMe), 4.4 (1H, dd, $J = 18, 7$ Hz, C_2-H), 4.7 (1H, dd, $J = 18, 3.5$ Hz, C_2-H), 6.27 (1H, dd, $J = 7, 3.5$ Hz, C_3-H), 7.2—8.2 (9H, m, ArH). *Anal.* Calcd for $C_{16}H_{15}ClO_4S$: C, 56.72; H, 4.46. Found: C, 56.49; H, 4.46.

Deprotonation of 2 with Strong Base——a) With Sodium Hydride in THF: Sodium hydride (142 mg, 2.95 mmol) was added to a solution of **2** (1 g, 2.95 mmol) in dry THF (50 ml) under a nitrogen atmosphere, and the mixture was stirred for 17 h at room temperature. The reaction mixture was concentrated to dryness under reduced pressure. Ether was added to the residue and ether-insoluble crystals were filtered off. The crystals were recrystallized from dichloromethane–ether to afford 110 mg (15.7%) of 1,6-bis(*o*-methylthiophenyl)-1,6-diphenyl-1,3,5-hexatriene (**4**) as yellow needles, mp 254—256 °C. IR (KBr): 3040, 1500, 1470, 1450, 1440, 765, 750, 690 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.32 (6H, s, SMe), 6.0—6.9 (4H, m, olefinic H), 7.0—7.5 (18H, m, ArH). MS *m*/*z*: 476 (M^+). *Anal.* Calcd for $C_{32}H_{28}S_2$: C, 80.63; H, 5.92. Found: C, 80.42; H, 5.70. The ether extracts were evaporated *in vacuo* and the residual oil was subjected to PLC on silica gel using benzene–hexane (1 : 1) to give 160 mg (22.8%) of a mixture of 2-methyl-4-phenyl-1-thio-2*H*-chromene (**5**) and 4-methyl-4-phenyl-1-thio-4*H*-chromene (**6**) as a pale brown oil, bp 105—110 °C (bath temp., 0.2 mmHg). ^{1}H-NMR ($CDCl_3$) δ of **5**: 1.45 (3H, d, $J = 7.5$ Hz, Me), 3.80 (1H, dq, $J = 7.5, 5.5$ Hz, C_2-H), 5.98 (1H, d, $J = 5.5$ Hz, C_3-H). ^{1}H-NMR ($CDCl_3$) δ of **6**: 1.75 (3H, s, Me), 5.90 (1H, d, $J = 10$ Hz, C_2-H), 6.40 (1H, d, $J = 10$ Hz, C_3-H). *Anal.* Calcd for $C_6H_{14}S$: C, 80.63; H, 5.92. Found: C, 80.44; H, 5.83. The ratio of **5** and **6** = 4 : 1.

b) With KOH in Ethanol: A solution of KOH (165 mg, 2.95 mmol) in dry ethanol (15 ml) was added by syringe under a nitrogen atmosphere to a stirred suspension of **2** (1 g, 2.95 mmol) in dry ethanol (20 ml), and the mixture was stirred for 15 h at room temperature. The reaction mixture was extracted with dichloromethane, dried over anhydrous $MgSO_4$, and evaporated. The residual solid was recrystallized from dichloromethane–ethanol to give 490 mg (68.3%) of **4** as pale yellow needles.

Desulfurization of 4——A mixture of **4** (482 mg, 1 mmol) and Raney Ni (W-2) (5 g) in ethanol (20 ml) was refluxed for 6 h. Acetone was added to the reaction mixture, and the solids were filtered off. The filtrate was concentrated to leave colorless crystals, which were recrystallized from dichloromethane–ethanol to afford 30 mg (7.7%) of 1,1,6,6-tetraphenylhexane (**7**) as colorless prisms, mp 125—127 °C (lit.[7] mp 118 °C). IR (KBr): 2900, 2820, 1600, 1490, 1450, 1350, 1070, 1035, 755, 745, 705 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.1—1.45 (4H, m, -CH_2-), 1.8—2.2 (4H, m, -CH_2-), 3.85 (2H, t, $J = 8$ Hz, C_1-H, C_6-H), 7.0—7.4 (20H, m, ArH).

1-Methyl-2,4,-diphenyl-1-thio-2*H*-chromenium Perchlorate (9)——Silver perchlorate (1.38 g, 6.57 mmol) was added portionwise to a stirred and ice-cooled solution of 2,4-diphenyl-1-thio-2*H*-chromene (**8**)[6] and methyl iodide (9.45 g, 65.7 mmol) in 1,2-dichloroethane (50 ml), and the mixture was stirred for 14 h. The precipitate was filtered off and the filtrate was concentrated *in vacuo* to dryness. The residue was dissolved in dichloromethane and diluted with ether to precipitate a mixture of yellow-colored and orange-colored crystals. The yellow-colored crystals were collected by hand and purified by repeated recrystallization from chloroform–ether to give 2.4 g (88.5%) of **9** as yellow needles, mp 161—163 °C (dec.). IR (KBr): 1090 cm^{-1} (ClO_4^-). ^{1}H-NMR ($CDCl_3$) δ: 3.45 (3H, s, SMe), 6.19 (1H, d, $J=7$ Hz, C_2-H), 6.41 (1H, d, $J=7$ Hz, C_3-H), 7.3—8.0 (14H, m, ArH). *Anal.* Calcd for $C_{22}H_{19}ClO_4S$: C, 63.69; H, 4.62. Found: C, 63.41; H, 4.61. The orange-red colored crystals were also purified by recrystallization from chloroform–ether to afford 50 mg (1.8%) of 2,4-diphenyl-1-thianaphthylium perchlorate (**10**) as orange-red needles, mp 239—241 °C (dec.) (lit.,[6] 228—229 °C (dec.)). The structure of **10** was confirmed by comparison of the spectral data with those of an authentic sample.[6] IR (KBr): 1090 (ClO_4^-) cm^{-1}. *Anal.* Calcd for $C_{21}H_{15}ClO_4S$: C, 63.24; H, 3.79. Found: C, 63.02; H, 3.78.

Reactions of 9 with Base——a) With KOH in Ethanol: A solution of KOH (135 mg, 2.41 mmol) in dry ethanol was added dropwise by syringe to a stirred solution of **9** (1 g, 2.41 mmol) in dry ethanol (20 ml) under a nitrogen atmosphere. After being stirred for 15 h, the reaction mixture was poured into water, and extracted with dichloromethane. The extracts were washed with water, dried over anhydrous $MgSO_4$, and evaporated under reduced pressure. The residual oil was subjected to PLC on silica gel using benzene–pet. ether (1 : 1) to give two fractions. The first fraction afforded 220 mg (25.3%) of a mixture of *Z*- (**11a**) and *E*-α-(2-methylthiophenyl)-β-ethoxyphenylmethylstyrene (**12a**) as a colorless oil, bp 190—200 °C (0.3 mmHg). IR (KBr): 1100 (C–O–C) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ of **11a** (or **12a**): 1.17 (3H, t, $J=7$ Hz, $OCH_2C\underline{H}_3$), 2.22 (3H, s, SMe), 3.20—3.80 (2H, m, $OC\underline{H}_2CH_3$), 4.68 (1H, d, $J=9$ Hz, CH), 6.38 (1H, d, $J=9$ Hz, olefinic H), 7.0—8.0 (14H, m, ArH). ^{1}H-NMR ($CDCl_3$) δ of **12a** (or **11a**): 1.17 (3H, t, $J=7$ Hz, $OCH_2C\underline{H}_3$), 2.35 (3H, s, SMe), 3.20—3.80 (2H, m, $OC\underline{H}_2CH_3$), 4.68 (1H, d, $J=9$ Hz, CH), 6.48 (1H, d, $J=9$ Hz, olefinic H), 7.0—7.8 (14H, m, ArH). The ratio of **11a** and **12a** was 0.9 : 1 on the basis of ^{1}H-NMR spectral data. The second fraction gave 150 mg (19.8%) of 1,6-bis(*o*-methylthiophenyl)-1,3,4,6-tetraphenyl-1,3,5-hexatriene (**13**) as yellow prisms, mp 210—211 °C. ^{1}H-NMR ($CDCl_3$) δ: 2.18 (6H, br s, 2 × SMe), 6.72—7.35 (30H, m, olefinic H and ArH). MS *m/z*: 628 (M$^+$). *Anal.* Calcd for $C_{44}H_{36}S_2$: C, 84.04; H, 5.76. Found: C, 84.14; H, 5.67.

b) With Sodium Hydride in THF: Sodium hydride (120 mg, 2.3 mmol) was added to a stirred solution of **9** (950 mg, 2.3 mmol) in dry THF (30 ml) under a nitrogen atmosphere, and the mixture was stirred for 3 h. The reaction mixture was poured into ice-water, and extracted with dichloromethane. The extract was washed with water, dried over anhydrous $MgSO_4$, and evaporated. The residue was purified by PLC on silica gel using benzene–pet. ether (1 : 1) to afford 470 mg (65.3%) of **13**.

c) With Triethylamine in Ethanol: Triethylamine (150 mg, 1.4 mmol) was added to a solution of **9** (300 mg, 0.7 mmol) in dry ethanol (10 ml), and the mixture stirred for 1 h, then poured into water and extracted with ether. The ether layer was washed with water, dried over anhydrous $MgSO_4$, and evaporated. The residue was purified by microdistillation to give 230 mg (88%) of a mixture of **11a** and **12a**.

d) With Triethylamine in Methanol: The same reaction as described in c) was performed by using methanol as a solvent instead of ethanol, and work-up as above afforded 200 mg (80%) of a mixture of *Z*- (**11b**) and *E*-α-(2-methylthiophenyl)-β-methoxyphenylmethyl styrene (**12b**) as a colorless oil, bp 180—190 °C (bath temperature) (0.3 mmHg). IR (KBr): 1095 (C–O–C) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ of **12a** (or **12b**): 2.2 (3H, s, SMe), 3.21 (3H, s, OMe), 4.45 (1H, d, $J=9$ Hz, CH), 6.33 (1H, d, $J=9$ Hz, olefinic H), 6.8—7.8 (14H, m, ArH). ^{1}H-NMR ($CDCl_3$) δ of **12b** (or **12a**): 2.35 (3H, s, SMe), 3.32 (3H, s, OMe), 4.55 (1H, d, $J=9$ Hz, CH), 6.45 (1H, d, $J=9$ Hz, olefinic H), 6.8—7.8 (14H, m, ArH). *Anal.* Calcd for $C_{23}H_{22}OS$: C, 79.73; H, 6.40. Found: C, 79.89; H, 6.34.

Treatment of 11a and 12a with Perchloric Acid——A 70% perchloric acid solution was added to a solution of a mixture of **11a** and **12a** (500 mg) in ether (30 ml), and the precipitates were filtered off and recrystallized from dichloromethane–ether to give 410 mg (71.3%) of **9**.

Desulfurization of 11a and 12a——A mixture of **11a** and **12a** (230 mg, 0.64 mmol) and Raney Ni (W-2, 2 g) in ethanol (30 ml) was refluxed for 6 h. Acetone was added to the reaction mixture and refluxed for 30 min to deactivate the remaining Raney Ni, and the mixture was filtered. The filtrate was evaporated to give an oil, which was purified by PLC on silica gel using benzene–pet. ether (1 : 1) as the solvent to afford 150 mg (74.4%) of 1-ethoxy-1,3,3-triphenylpropane (**14a**) as a colorless oil, bp 160—165 °C (bath temperature) (0.2 mmHg). ^{1}H-NMR ($CDCl_3$) δ: 1.14 (3H, t, $J=7$ Hz, $OCH_2C\underline{H}_3$), 2.2—2.5 (2H, m, $-CH_2-$), 2.98—3.50 (2H, m, $OC\underline{H}_2CH_3$), 4.02 (1H, dd, $J=8$, 5.5 Hz, CH), 4.23 (1H, dd, $J=9$, 8 Hz, CH), 6.8—7.8 (15H, m, ArH). *Anal.* Calcd for $C_{23}H_{24}O$: C, 87.30; H, 7.65. Found: C, 87.26; H, 7.67.

Desulfurization of 11b and 12b——A mixture of **11b** and **12b** (570 mg, 1.65 mmol) was subjected to desulfurization with Raney Ni (W-2, 6 g) as described above and 380 mg (76.2%) of 1-methoxy-1,3,3-triphenylpropane (**14b**) was obtained as a colorless oil, bp 165—170 °C (bath temperature) (0.3 mmHg). ^{1}H-NMR ($CDCl_3$) δ: 2.25—2.70 (2H, m, $-CH_2-$), 3.14 (3H, s, OMe), 3.89 (1H, dd, $J=7.5$, 6 Hz, CH), 4.18 (1H, dd, $J=9$, 7 Hz, CH), 7.05—7.55 (15H, m, ArH).

2-Cyano-4-phenyl-1-thio-2*H*-chromene (18)——Powdered 4-phenyl-1-thianaphtylium perchlorate[6] (**17**, 5 g, 16 mmol) was added in small portions with stirring to a mixture of sodium cyanide (1.5 g, 23 mmol), water (1.5 ml) and dichloromethane (150 ml), and the mixture was further stirred for 14 h at room temperature. The organic layer was separated, washed with water, and dried over anhydrous potassium carbonate. The solvent was evaporated off under reduced pressure to give 3.52 g (91.2%) of **18**, which was recrystallized from dichloromethane–pet. ether to form colorless needles, mp 114 °C. IR (KBr): 2220 (CN) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 4.4 (1H, d, $J=7.5$ Hz, C_2-H), 6.04 (1H, d, $J=7.5$ Hz, C_3-H), 7.1—7.8 (9H, m, ArH). *Anal.* Calcd for $C_{16}H_{11}NS$: C, 77.08; H, 4.45; N, 5.62. Found: C, 77.17; H, 4.45; N, 5.35.

2-Cyano-1-methyl-4-phenyl-1-thio-2*H*-chromenium Perchlorate (19)——Silver perchlorate (566 mg, 2.7 mmol) was added portionwise with stirring to an ice-cooled solution of **18** (680 mg, 2.7 mmol) and methyl iodide (3.9 g, 27 mmol) in dichloromethane (30 ml). After being stirred for 14 h, the reaction mixture was filtered. The precipitates were washed with acetonitrile several times. The washings and the filtrate were combined and evaporated under reduced pressure to give the crystals, which were recrystallized from dichloromethane–ether to afford 830 mg (83.7%) of **19** as colorless prisms (inseparable mixture of *cis* and *trans* stereoisomers), mp 180 °C (dec.). IR (KBr): 2240 (CN), 1080 (ClO_4^-) cm^{-1}. ^{1}H-NMR (CF_3CO_2H) δ: 3.48 (s, SMe), 5.88 (d, $J=7.5$ Hz, C_2-H), and 6.42 (d, $J=7.5$ Hz, C_3-H), which are attributable to one of the isomers; 3.54 (s, SMe), 6.15 (d, $J=4.5$ Hz, C_2-H), and 6.30 (d, $J=4.5$ Hz, C_3-H), which are assignable to the other isomer. *Anal.* Calcd for $C_{17}H_{14}ClNO_4S$: C, 56.12; H, 3.88; N, 3.85. Found: C, 56.12; H, 3.95; N, 3.65.

2-Cyano-1-methyl-4-phenyl-1-thianaphthalene (20)——Triethylamine (950 mg, 4.7 mmol) was added to a stirred suspension of **19** (1.71 g, 4.7 mmol) in ethanol (50 ml) at room temperature, and the mixture was further stirred for 1 h, then poured into water and extracted with benzene. The extract was washed with water, dried over anhydrous $MgSO_4$, and evaporated to dryness under reduced pressure. The residual oil was triturated with ether to give 1.22 g (98.4%) of **20** as yellow prisms after recrystallization from dichloromethane–ether, mp 137—139 °C (dec.). IR (KBr): 2170 (CN) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.26 (3H, s, SMe), 6.80 (1H, s, C_3-H), 7.20—7.60 (9H, m, ArH). *Anal.* Calcd for $C_{17}H_{13}NS$: C, 77.53; H, 4.98; N, 5.32. Found: C, 77.34; H, 4.88; N, 5.13.

Thermal Rearrangement of 20——A solution of **20** (520 mg, 2 mmol) in acetone (30 ml) was refluxed for 50 h. The solvent was evaporated off, and the residual oil was subjected to column chromatography on silica gel using benzene–pet. ether (1 : 1) to give the following two products: 2-cyano-2-methyl-4-phenyl-1-thio-2*H*-chromene (**21**) (186 mg, 26.6%), colorless oil. IR (KBr): 2240 (CN) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.94 (3H, s, Me), 5.82 (1H, s, C_3-H), 7.05—7.60 (9H, m, ArH). *Anal.* Calcd for $C_{17}H_{13}NS$: C, 77.53; H, 4.98; N, 5.32. Found: C, 77.33; H, 4.96; N, 5.18. 2-Cyano-4-methyl-4-phenyl-1-thio-4*H*-chromene (**22**) (93 mg, 13.3%), colorless oil. IR (KBr): 2238 (CN) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.82 (3H, s, Me), 6.80 (1H, s, C_3-H), 6.90—7.48 (9H, m, ArH). *Anal.* Calcd for $C_{17}H_{13}NS$: C, 77.53; H, 4.98; N, 5.32. Found: C, 77.82; H, 5.06; N, 5.25.

Reaction of 20 with 19——A mixture of **20** (220 mg, 0.6 mmol) and **19** (160 mg, 0.6 mmol) in acetonitrile (30 ml) was stirred at room temperature for 30 min. The precipitated solids were recrystallized from acetone–pet. ether to give 120 mg (37.6%) of 3,4-dicyano-1,6-bis(2-methylthiophenyl)-1,6-diphenyl-1,3,5-hexatriene (**23**) as orange needles, mp 279—280 °C. IR (KBr): 2225 (CN) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.47 (3H, s, Me), 7.10—7.65 (10H, m, ArH and olefinic H). MS *m/z*: 526 (M^+). *Anal.* Calcd for $C_{34}H_{26}N_2S_2$: C, 77.53; H, 4.98; N, 5.32. Found: C, 77.45; H, 4.92; N, 5.11.

Reaction of 20 with Tetracyanoethylene——A mixture of **20** (270 mg, 1 mmol) and tetracyanoethylene (130 mg, 1 mmol) in benzene (25 ml) was stirred for 12 h under an N_2 atmosphere at room temperature. The solvent was evaporated off *in vacuo* to give a dark red oil, from which tetracyanoethylene was recovered as crystals. The oil was subjected to PLC on silica gel using benzene as the solvent to give 25 mg (9.3%) of **23**.

Reaction of 20 with 4-Phenyl-1-thianaphthylium Perchlorate (17)——A solution of the perchlorate (**17**, 1.18 g, 3.7 mmol) in dichloromethane (10 ml) was added to a stirred solution of **20** (530 mg, 2 mmol) in dichloromethane (30 ml), and the mixture was stirred for 6 h. The solvent was evaporated off under reduced pressure to precipitate 910 mg (77.2%) of **17**. The filtrate was concentrated to dryness to leave an oil which was separated by column chromatography on alumina. The obtained crystals were recrystallized from dichloromethane–ether to give 140 mg (30.4%) of **23** as orange needles.

Reaction of 20 with Maleic Anhydride——A solution of maleic anhydride (280 mg, 2.9 mmol) in benzene (10 ml) was added to a stirred solution of **20** (500 mg, 1.9 mmol) in benzene (25 ml) and the mixture was warmed to 40 °C for 30 h. The reaction mixture was concentrated to dryness. The residue was purified by PLC on silica gel using dichloromethane–pet. ether (1 : 1) as the solvent to afford 30 mg (6%) of **23** as orange needles.

Reaction of 20 with DMAD——A mixture of **20** (1.7 g, 6.3 mmol) and DMAD (1.7 g, 12.6 mmol) in benzene (100 ml) was stirred for 10 h at room temperature. The reaction mixture was concentrated *in vacuo* to dryness to give a dark red oil. The oil was separated by column chromatography on silica gel using hexane–benzene to afford colorless crystals, which were recrystallized from ether to give 300 mg (12%) of 5-cyano-3,4-bis(methoxycarbonyl)-7-phenyl-2,3-dihydro-1-benzothionin (**27**) as colorless prisms, mp 147—149 °C. IR (KBr): 2220 (CN), 1740 and 1710 (ester carbonyl groups) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.98 (1H, dd, $J=15$, 9 Hz, one of C_2-H), 3.68 (3H, s, OMe), 3.71 (1H, br d, $J=15$ Hz, the other of C_2-H), 3.72 (3H, s, OMe), 4.20 (1H, br d, $J=9$ Hz, C_3-H), 6.90 (1H, s, olefinic H), 7.20—8.00 (9H, m, ArH). MS *m/z*: 405 (M^+). *Anal.* Calcd for $C_{23}H_{19}NO_4S$: C, 68.13; H, 4.72; N, 3.45. Found: C, 68.12; H, 4.79;

N, 3.38. *m*-Chloroperbenzoic acid (20 mg) was added to a stirred and ice-cooled solution of **27** (30 mg) in dichloromethane (10 ml), and the mixture was stirred at room temperature for 12 h. The reaction mixture was washed with an aqueous $NaHCO_3$ solution, dried over $MgSO_4$ and evaporated down *in vacuo* to give 25 mg (77.8%) of 5-cyano-3,4-bis(methoxycarbonyl)-7-phenyl-2,3-dihydro-1-benzothionin 1,1-dioxide (**28**) as colorless prisms after recrystallization from ether, mp 192—193 °C. IR (KBr): 2225 (CN), 1740 (CO), 1318, 1058 (SO_2) cm^{-1}. ^1H-NMR ($CDCl_3$) δ: 3.45 (1H, dd, $J=17$, 10 Hz, one of C_2-H), 3.78 (6H, s, 2 × OMe), 4.28 (1H, br d, $J=17$ Hz, the other of C_2-H), 4.50 (1H, br d, $J=10$ Hz, C_3-H), 6.83 (1H, s, olefinic H), 7.30—8.30 (9H, m, ArH). *Anal.* Calcd for $C_{23}H_{19}NO_6S$: C, 63.15; H, 4.38; N, 3.20. Found: C, 63.00; H, 4.38; N, 3.08.

References and Notes

1) *a)* M. Hori, T. Kataoka, H. Shimizu, K. Narita, S. Ohno, and H. Aoki, *Chemistry Lett.*, **1974**, 1101; *b)* M. Hori, T. Kataoka, H. Shimizu, S. Ohno, K. Narita, H. Takayanagi, H. Ogura, and Y. Iitaka, *Tetrahedron Lett.*, **1979**, 4315; *c)* M. Hori, T. Kataoka, H. Shimizu, S. Ohno, K. Narita, and H. Koyama, *J. Chem. Soc., Chem. Commun.*, **1981**, 364.
2) *a)* M. Hori, T. Kataoka, H. Shimizu, S. Ohno, and K. Narita, *Tetrahedron Lett.*, **1978**, 251; *b)* M. Hori, T. Kataoka, H. Shimizu, and S. Ohno, *ibid.*, **1978**, 255; *c) Idem, J. Org. Chem.*, **45**, 2468 (1980); *d)* S. Ohno, H. Shimizu, T. Kataoka, and M. Hori, *ibid.*, **49**, 2472 (1984).
3) *a)* M. Hori, T. Kataoka, H. Shimizu, and O. Komatsu, *J. Chem. Soc., Chem. Commun.*, **1985**, 883; *b)* M. Hori, T. Kataoka, H. Shimizu, O. Komatsu, and K. Hamada, *J. Org. Chem.*, **52**, 3668 (1987).
4) For a preliminary communication of a portion of this work, see: M. Hori, T. Kataoka, H. Shimizu, and H. Aoki, *Heterocycles*, **5**, 413 (1976).
5) A. G. Hortmann, R. L. Harris, and J. A. Miles, *J. Am. Chem. Soc.*, **96**, 6119 (1974).
6) A. Lüttringhaus, N. Engelhard, and A. Kolb, *Justus Liebigs Ann. Chem.*, **654**, 189 (1962).
7) B. Angelo, *Bull. Soc. Chim. Fr.*, **5**, 1710 (1969).
8) W. T. Flowers, G. Holt, and M. A. Hope, *J. Chem. Soc., Perkin Trans. 1*, **1974**, 1116.
9) G. Suld and C. C. Price, *J. Am. Chem. Soc.*, **84**, 2090 (1962).