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Synthesis and Thermal Reactions of Cyano-Stabilized Cyclic Sulfur Ylides, 2-Alkyl-1-cyano-3,4-dihydro-1*H*-2-thionianaphthalen-1-ides

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1-Cyanoisothiochromans **4** were synthesized by the intramolecular Pummerer reaction of cyanomethyl phenethyl sulfoxides **3** with trifluoroacetic anhydride. Alkylation of the isothiochromans **4** afforded isothiochromanium salts **5** which consist of *cis*- and *trans*-isomers. 1-Cyano-2-methyl-3,4-dihydro-1*H*-2-thionianaphthalen-1-ides **6** were prepared by deprotonation of **5** with triethylamine or sodium hydride. Thermal reaction of the ylide **6a** in benzene or *N*,*N*-dimethylformamide gave the 1,2-rearranged product **7** accompanied with the dimers **8**, whereas the reaction in acetonitrile gave the dimers *E*-**8** (**8**-I) (31.6%) and *Z*-**8** (**8**-II) (22.6%) as the major products. The geometrical structures of **8** were determined by infrared (IR) and Raman spectroscopy. The dimers **8** were formed at room temperature by treatment with tetracyanoethylene or 7,7,8,8-tetracyanoquinodimethane. Unexpected products, 1-benzylated isothiochromans **10**, were obtained upon heating **6a** in toluene and its derivatives. A reaction mechanism involving the benzyl radicals was postulated for this novel solvent-uptake reaction.

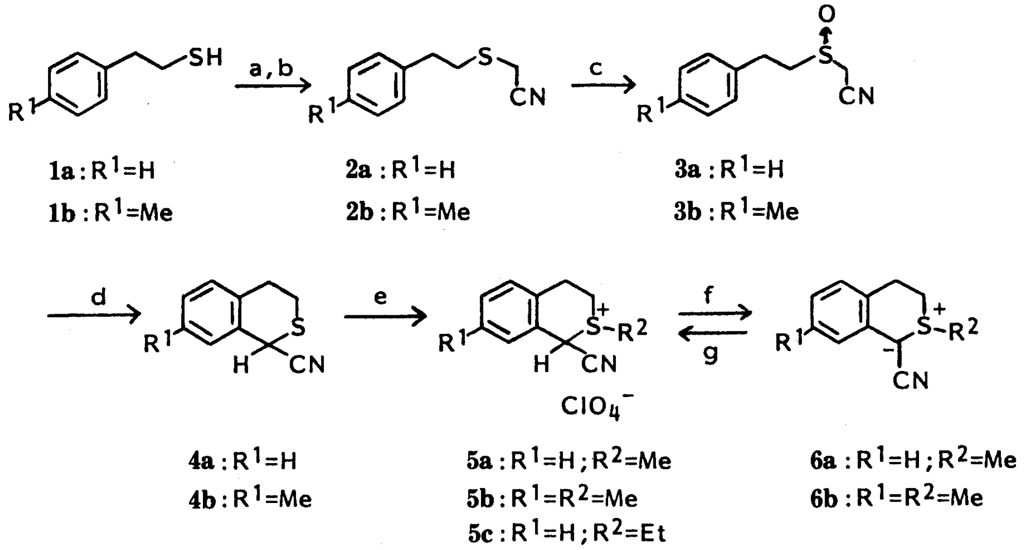
Keywords——Pummerer reaction; thermal reaction; dimerization; Stevens-type rearrangement; solvent uptake; sulfur ylide; 3,4-dihydro-1*H*-2-thionianaphthalen-1-ide; isothiochroman; 1,2-dicyanoethene; Raman spectrum

Sulfur ylides are stabilized by an electron-withdrawing group. A wide variety of carbonyl-stabilized sulfur ylides have been synthesized, but only a few cyano-stabilized sulfur ylides are known. We have studied cyano-stabilized cyclic sulfur ylides such as 1-alkyl-2-cyano-1-thionianaphthalen-2-ides (1-thianaphthalenes),$^{1)}$ 2-alkyl-1-cyano-2-thionianaphthalen-1-ides (2-thianaphthalenes),$^{2)}$ 9-cyano-10-methyl-10-thioniaanthracen-9-ide (10-thiaanthracene),$^{3)}$ and 9-alkyl-10-cyano-9-thioniaphenanthren-10-ides (9-thiaphenanthrenes)$^{4)}$ in relation to thiabenzenes. These compounds undergo thermal [1,2]- or [1,4]-rearrangement and novel ring-transformation reactions involving a rearrangement.

The C(3)–C(4) double bond in 2-thianaphthalenes contributes to their stabilization and participates in some reactions with electrophiles.$^{2)}$ 3,4-Dihydro-1*H*-2-thionianaphthalen-1-ides (3,4-dihydro-2-thianaphthalenes) without the C(3)–C(4) double bond would be more reactive than 2-thianaphthalenes and interesting reactions can be expected. The corresponding benzoyl-stabilized ylides, on the other hand, underwent interesting S–O 1,4-rearrangement and unique ring-opening reactions.$^{5)}$ This report describes the synthesis and thermal reactions of 1-cyano-3,4-dihydro-2-thianaphthalenes.$^{6)}$

Synthesis

The synthesis of 2-alkyl-1-cyano-3,4-dihydro-2-thianaphthalenes is outlined in Chart 1. Reaction of chloroacetonitrile with 2-arylethanethiols (**1**) in the presence of sodium ethoxide provided 2-arylethylthioacetonitriles (**2**), which were oxidized with sodium periodate or *m*-



a: NaOEt, b: $ClCH_2CN$, c: $NaIO_4$ or MCPBA, d: $(CF_3CO)_2O$,

e: R^2I-$AgClO_4$, f: Et_3N or NaH, g: $HClO_4$

Chart 1

chloroperbenzoic acid (MCPBA) to give the sulfoxides (**3**). The intramolecular Pummerer reaction of **3** with trifluoroacetic anhydride afforded 1-cyanoisothiochromans (**4**) in high yields. This procedure is superior to the known synthetic method of **4a** involving the reaction of unstable 1-chloroisothiochroman with mercuric cyanide, since the waste mercury causes pollution.[7] The isothiochromans (**4**) were alkylated with alkyl iodides and silver perchlorate to give 2-alkyl-1-cyanoisothiochromanium perchlorates (**5**). Stereoisomers were not detected by nuclear magnetic resonance (NMR) measurement immediately after dissolving **5a** in trifluoroacetic acid. However, after the solution had been allowed to stand overnight at room temperature or warmed in a water-bath, isomerization was recognized. The proton nuclear magnetic resonance (^{1}H-NMR) spectra showed two pairs of singlets at δ 2.83 (SCH_3) and 5.97 (1-H) for the major isomer, and at δ 3.06 (SCH_3) and 5.86 (1-H) for the other isomer. Similar phenomena were found in other sulfonium salts (**5b, c**) (see Experimental). The signal of a substituent occupying the *cis* configuration with respect to the cyano group appears at lower field than that of a *trans*-substituent. Therefore the minor isomers exhibiting a lower S-methyl signal were assigned as the *cis*-isomers and the major isomers were assigned as the *trans*-isomers.

Ylides (**6a, b**) were prepared by treatment of the sulfonium salts (**5a, b**) with triethylamine. The ylides (**6a, b**) showed no signal due to 1-H in the ^{1}H-NMR spectra and showed a broad and strong absorption at 2120 cm^{-1}, shifted to lower frequency, due to the characteristic ylidic cyano group in the infrared (IR) spectra. Treatment of **6a** with perchloric acid afforded the sulfonium salt (**5a**) in 84.8% yield.

Thermal Reactions

The thermal reaction did not proceed in dichloromethane. Even when **6a** was refluxed for 12 h in acetonitrile, it was recovered in 39.7% yield. This finding indicates that the ylide **6a** is rather stable in acetonitrile and a long time is necessary to complete the thermal reaction. The ylide **6a** produced a mixture of 1,2-dicyano-1,2-bis[*o*-(2-methylthioethyl)phenyl]ethenes (**8**) in 54.2% and a rearranged compound, 1-cyano-1-methylisothiochroman (**7**), in 8.6% yield upon

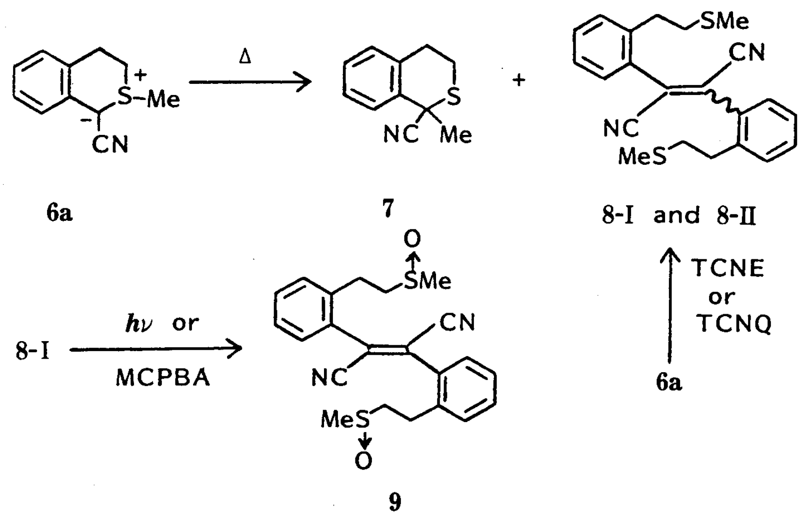


Chart 2

Table I. Thermal Reactions of 1-Cyano-2-methyl-3,4-dihydro-2-thianaphthalene (**6a**)

Solvent	Time	Temperature	Product (yield: %)
Acetonitrile	60 h	Reflux	**7** (8.6), **8**-I (22.6), **8**-II (31.6)
N,*N*-Dimethylformamide	2 h	Reflux	**7** (39.1), **8**-II (5.4)
Benzene	5 h	Reflux	**4a** (11), **7** (39), **8**-I (4.6), **8**-II (10.8)
Toluene	4 h	Reflux	**4a** (4.8), **7** (35.2), **10a** (23.2)
p-Xylene	2.5 h	Reflux	**4a** (18.6), **7** (11),[b] **8** (15.5),[a] **10b** (18)[b]
p-Methoxytoluene	10 min	140—148 °C	**7** (40.3), **8** (9),[a,b] **10c** (9)[b]
p-Nitrotoluene	10 min	145—150 °C	**7** (15.5), **8** (24.3)[a]

a) A mixture of *Z*- and *E*-isomers. *b*) These compounds could not be separated by preparative TLC and the yields were calculated on the basis of the intensities of methyl group signals in the ^{1}H-NMR spectrum of the mixture.

heating in dry acetonitrile for 84 h. In contrast, thermal reactions of **6a** in *N*,*N*-dimethylformamide yielded the rearranged product **7** in 39.1% yield and a mixture of the dimers **8** in 5.4% yield. The 1,2-rearranged product **7** was identical with a sample synthesized independently with regard to the IR and NMR spectra.[8] The dimers **8** were separated by preparative thin-layer chromatography (TLC) into two isomers (**8**-I) and (**8**-II), which were presumed to be the *Z* and *E* isomers on the basis of their MS fragmentation patterns and the chemical shifts in their carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectra. However, we did not determine which is *E* or *Z* by way of ^{1}H-, ^{13}C-NMR and ultraviolet (UV) spectroscopy and chemical derivation with concentrated sulfuric acid. These methods had been used for the structure determination of geometrical isomers of 1,2-dicyanoethenes.[9] *E*-Olefins isomerize photochemically to *Z*-isomers, and *Z*-isomers undergo the reverse photoisomerization in the presence of halogen.[10] Exposure of *E*-**8** (**8**-II) to sunlight afforded a disulfoxide **9** in 18.4% yield and did not afford the isomerized product *Z*-**8** (**8**-I). The photooxidized product **9** was identical with an authentic specimen prepared by oxidation of **8**-II with MCPBA. The geometry of the tetra-substituted ethenes **8** was determined by comparison of the IR and Raman spectra of the geometrical isomers, as will be described later.

Sulfur ylides decompose thermally or photochemically to form sulfides and olefins or cyclopropanes. Three different reaction mechanisms have been proposed for the formation of these products. Several reports claimed carbene intermediates for dimerization or cyclopropanation.[11] Dimethylsulfonium phenacylide reacts thermally with the corresponding sulfonium salt to give tribenzoylcyclopropane.[11c,12] Stable sulfur ylides decompose at 35 °C in the presence of a disulfide or thiocyanogen to form the decomposition products of ylides, sulfides and olefins or cyclopropanes.[13]

We performed several experiments to investigate the mechanism of formation of the dimers (**8**). When a solution of the ylide **6a** in acetonitrile was refluxed in the presence of cyclohexene for 2 d or in cyclohexene for 1.5 h no norcarane derivative was obtained. A solution of **6a** and the corresponding sulfonium salt **5a** in dichloromethane was refluxed for 21 h to afford **8**-I and **8**-II in 10% and 48% yields, respectively. It has been reported that moisture protonates dimethylsulfonium phenacylide to form a sulfonium salt and the sulfonium salt reacts with the ylide to give 1,2,3-tribenzoylcyclopropane *via* 1,2-dibenzoylethene.[11c] However, the ylide **6a** was recovered together with a trace amount of the dimer **8** upon refluxing a solution of **6a** in acetone or benzene containing water. From these experiments, it was concluded that the sulfonium salt **5a** was not formed even in the presence of water, and the dimers **8** were not formed. The thermal dimerization occurred more easily in acetonitrile than in benzene, although the boiling points of these solvents are very similar. This finding implies that the ylides interact with acetonitrile. We assumed that electrostatic interaction or charge transfer interaction would be present between them, and we examined the following reactions. Treatment of **6a** with 0.1 mol eq of tetracyanoethylene or 7,7,8,8-tetracyanoquinodimethane in dichloromethane gave the dimers **8** in good yields even at room temperature.

Next, we examined thermal reactions of the ylides **6** in toluene and found an interesting solvent-uptake reaction. The ylide **6a** yielded 1-benzyl-1-cyanoisothiochroman (**10a**) together with the 1,2-rearranged product **7** and the demethylated product **4a**. The structure of the unexpected product (**10a**) was judged to be 1-benzyl-1-cyanoisothiochroman from the following data: IR 2200 cm^{-1} (CN); ^{1}H-NMR δ: 3.49 (2H, AB q, $\Delta\nu = 20.0$ Hz, $J = 13.5$ Hz, PhCH$_2$); MS m/z: 265 and elemental analysis $C_{17}H_{15}NS$. This was confirmed by comparison with an authentic sample.[14] The [1,2]-thermal rearrangement of sulfur ylides is a radical reaction and sometimes involves radical coupling.[15] However, it has not previously been known that an aprotic solvent can be taken up during the rearrangement. Therefore, the thermal reaction was examined in other toluene derivatives, and the results are shown in Table I. 1-(*p*-Substituted benzyl)isothiochromans **10b, c** were obtained from the reactions in *p*-

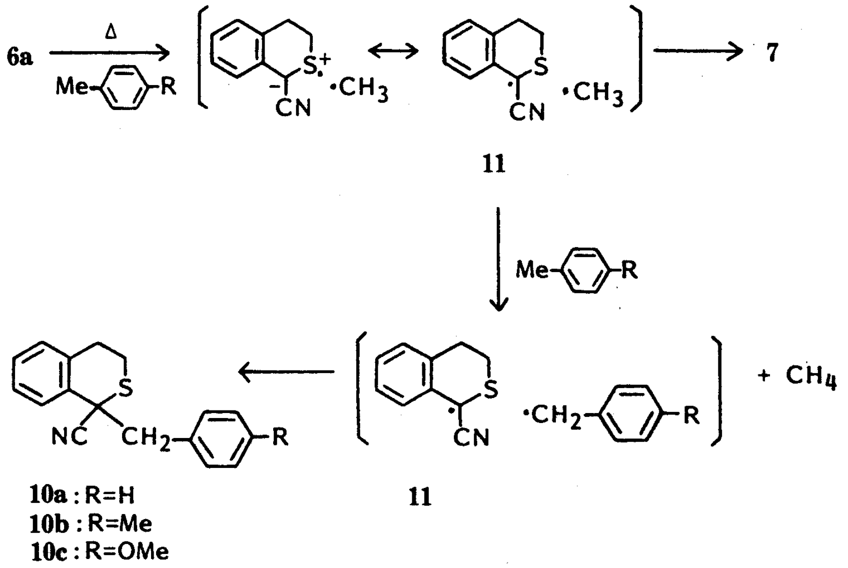


Chart 3

TABLE II. C$\equiv$N and C$=$C Stretching Frequencies (cm^{-1}) of 1,2-Dicyanoethenes

Compound	$\nu_{C\equiv N}$		$\nu_{C=C}$	
	IR	Raman	IR	Raman
Maleonitrile				
Liquid	2250 2231	2248$^{a)}$ 2228	1597	1596
CHCl$_3$ soln.	2250 2230	2251 2231	1598	1598
Fumaronitrile				
Solid$^{b)}$	2238	2228	—$^{c)}$	1607
CHCl$_3$ soln.	2241	2229	1612$^{d)}$	1612
8-I				
Solid$^{b)}$	2214	2214	1579	1580
CHCl$_3$ soln.	2221		1577	
8-II				
Solid$^{b)}$	2224	2217	—$^{c)}$	1593
CHCl$_3$ soln.	2226		—$^{c)}$	

a) A shoulder. *b*) For the IR spectrum in a KBr disk. *c*) Not observed. *d*) A very weak band.

xylene and 4-methylanisole in yields of 18% and 9%, respectively, but 1-cyano-1-(*p*-nitrobenzyl)isothiochroman (**10d**) was not obtained from the reaction in *p*-nitrotoluene. The reason why **10d** was not formed is unclear so far.

Since the Stevens-type [1,2]-rearrangement is well-known to proceed *via* the radical pair intermediate,[15] we postulate a reaction pathway in which toluene is taken up as the benzyl radical (Chart 3). Methyl radical formed by the radical fission of the ylide **6a** abstracts a hydrogen of the methyl group of toluene and its derivatives. The benzyl radicals thus generated couple with 1-cyanoisothiochromanyl radical (**11**) to afford 1-(substituted benzyl)isothiochroman derivatives (**10a**—**c**).

Structure Determination of 1,2-Dicyano-1,2-bis[*o*-(2-methylthioethyl)phenyl]ethenes 8

Fumaronitrile and maleonitrile can be used as model compounds for the determination of the *Z* and *E* configurations in the 1,2-dicyanoethenes **8**-I and **8**-II by vibrational spectroscopy. Generally, when a molecule has a center of symmetry (inversion center), the mutual exclusion rule holds for the IR and Raman spectra.[16] Fumaronitrile possesses an inversion center.[17] Its IR and Raman bands will not be observed at the same frequencies. Vibrations symmetric to the inversion center will not be seen in the IR spectrum, but will appear in the Raman spectrum. Antisymmetric vibrations will be IR-active but Raman-inactive. On the other hand, since maleonitrile has the *Z* configuration, all the IR bands will be observed at the same frequencies as in the Raman spectrum.

In the present work the C$\equiv$N and C$=$C stretching vibrations were used for spectral comparison, since the former vibration gives rise to a sharp band which permits accurate determination of the observed frequency and the activity of the latter vibration depends on the molecular symmetry. Table II lists these frequencies of 1,2-dicyanoethenes including maleonitrile and fumaronitrile. The C$=$C stretching band can easily be assigned in the Raman spectra since this vibration gives the strongest band in the region of 1650—1550 cm^{-1}. The Raman data for chloroform solutions of **8**-I and **8**-II are not given in Table II; their Raman spectra were measured, but the observed solution spectra were not reliable, because the laser beam tended to decompose these compounds in chloroform solution.

As expected, a good match is obtained between the frequencies in the IR and Raman spectra of liquid maleonitrile, whereas there is no coincidence in the two spectra of fumaronitrile. The latter compound shows a difference of 10 cm^{-1} for the C$\equiv$N band in the crystalline state. Its C$=$C stretching band is not observed in the solid-state IR spectrum, but the corresponding Raman band appears at 1607 cm^{-1}.

For compound **8**-I the C$\equiv$N and C$=$C stretching frequencies in the IR spectrum agree with those in the Raman spectrum. In this compound no interaction between the two C$\equiv$N groups occurs, in contrast with the case of maleonitrile, and a singlet is observed at 2214 cm^{-1}. On the other hand, compound **8**-II gives an IR C$\equiv$N band which is a little different in frequency from the Raman band. A difference of 7 cm^{-1} is significant in relation to the frequency accuracy of the spectrometers used. Furthermore, this compound does not show any C$=$C stretching band in the IR spectrum, but has a strong Raman counterpart at 1593 cm^{-1}. These findings indicate the existence of a center of symmetry, at least in the ethene moiety including the C$\equiv$N groups. It is generally known that the C$=$C stretching frequencies of *Z* isomers are somewhat lower than those of the corresponding *E* compounds.[18] This rule holds for the C$=$C bands of maleonitrile and fumaronitrile, as seen from Table II. Those of the compounds **8**-I and **8**-II also follow this general rule. From these results, it is concluded that compound **8**-I has the *Z* configuration and compound **8**-II, the *E* form.

Experimental

Melting points were taken on a Yanagimoto micromelting point apparatus and are uncorrected. ^{1}H-NMR spectra were determined with a Hitachi R-20B spectrometer and chemical shifts are given in parts per million relative to tetramethylsilane as an internal standard. Mass spectra (MS) were recorded with a JEOL JMSD-300 spectrometer and high-resolution MS with the JMA 2000 on-line system. IR spectra were measured with a JASCO IRA-1 spectrometer. The IR and Raman spectra of 1,2-dicyanoethenes including maleonitrile and fumaronitrile were recorded on a JASCO 403G IR spectrometer and a Spex Ramalog 9 Raman spectrometer (excitation line: 488.0 or 514.5 nm of an argon ion laser), respectively, for the structural determination of the geometrical isomers. Methylcyclohexane and 1,2,4-trichlorobenzene were used as calibrants[19] in the region of 3000—2000 cm^{-1} of the IR spectra. In both spectra the frequency accuracy was estimated to be ± 1 cm^{-1}.

Maleonitrile was prepared from maleamide by the method described in the literature[20] and purified by column chromatography on silica gel and distillation under reduced pressure; bp 73 °C/5 mmHg. Fumaronitrile was purified by recrystallization of a commercial product from benzene–petroleum ether.

(2-Phenylethylthio)acetonitrile (2a)——2-Phenylethanethiol (10.0 g, 7.2 mmol) was added to a cooled solution of sodium ethoxide [prepared from sodium (1.7 g, 7.2 mmol) in ethanol (30 ml)] under a nitrogen atmosphere. A solution of chloroacetonitrile (5.5 g, 7.3 mmol) in ethanol (30 ml) was added to the solution of sodium 2-phenylethanethiolate. The reaction mixture was stirred for 5 h at room temperature, then the precipitate was filtered off and the filtrate was concentrated under reduced pressure. The residual oil was dissolved in ether, washed with water and dried ($MgSO_4$). The solvent was evaporated off and the residual oil (11.30 g) was used without further purification. IR ν_{max}^{neat} cm^{-1}: 2240 (CN). ^{1}H-NMR ($CDCl_3$) δ: 2.88 (4H, s, CH_2CH_2), 3.06 (2H, s, SCH_2CN), 7.20 (5H, s, PhH). MS *m/z*: 177 (M^+).

(2-*p*-Tolylethylthio)acetonitrile (2b)——A mixture of 2-(*p*-tolyl)ethyl bromide (15.1 g, 75.8 mmol) and thiourea (5.8 g, 75.8 mmol) in ethanol (30 ml) was refluxed for 3 h and cooled. An NaOH solution [prepared from NaOH (4.5 g) in water (20 ml)] was added to the mixture and the whole was refluxed for 2 h. A solution of chloroacetonitrile (5.7 g, 75.8 mmol) in *N*,*N*-dimethylformamide (DMF) (30 ml) was added to the solution of sodium 2-(*p*-tolyl)ethanethiolate thus prepared. The reaction mixture was then warmed at 80 °C for 2 h. The cooled mixture was poured into water and extracted with benzene–hexane (4 : 1), then the extracts were dried ($MgSO_4$) and concentrated. The residual oil was chromatographed on silica gel using chloroform–hexane (1 : 1) to give an oil (9.2 g, 63.4%). IR ν_{max}^{neat} cm^{-1}: 2240 (CN). ^{1}H-NMR ($CDCl_3$) δ: 2.31 (3H, s, CH_3), 2.96 (4H, s, CH_2CH_2), 3.19 (2H, s, SCH_2CN), 7.12 (4H, s, ArH). High resolution MS *m/z*: Calcd for $C_{11}H_{13}NS$: 191.0767. Found: 191.0752.

Cyanomethyl 2-Phenylethyl Sulfoxide (3a)——(a) MCPBA (85% pure) (12.94 g, 63.7 mmol) was gradually added to a cold solution of **2a** (11.30 g) with stirring. The mixture was stirred for 5 h at room temperature and then cooled in an ice-bath. A saturated $NaHCO_3$ solution (20 ml) was added and the whole was stirred for 30 min. The organic layer was separated, washed with water and dried ($MgSO_4$). The solvent was evaporated off and ether was added to the residue. The crystalline solid was collected and recrystallized from CH_2Cl_2–ether to give colorless plates (8.65 g, 70.2%), mp 58—59 °C. IR ν_{max}^{KBr} cm^{-1}: 2240 (CN), 1040 (S–O). ^{1}H-NMR ($CDCl_3$) δ: 3.10—3.25 (4H, m, CH_2CH_2), 3.62 (2H, AB q, $\Delta\nu = 11.7$ Hz, $J = 15.8$ Hz, CH_2CN), 7.28 (5H, brs, ArH). MS *m/z*: 193 (M^+). *Anal.* Calcd for $C_{10}H_{11}NOS$: C, 62.15; H, 5.74; N, 7.25. Found: C, 62.00; H, 5.77; N, 7.28. (b) A solution of sodium periodate (1.33 g, 6.21 mmol) in water (20 ml) was added to a solution of **2a** (1 g, 5.64 mmol) with cooling in an ice-bath. The reaction mixture was stirred for 30 h at room temperature. The precipitate was filtered off and the filtrate was poured into water and extracted with CH_2Cl_2. The extracts were dried ($MgSO_4$) and concentrated to dryness. Ether was added to the residue, and the resulting crystalline solid was collected and recrystallized. This sample was identical with the specimen prepared by method (a).

Cyanomethyl 2-(*p*-Tolyl)ethyl Sulfoxide (3b)——The sulfide **2b** (7.5 g, 39.2 mmol) was oxidized with MCPBA (85% pure) (7.5 g, 37.0 mmol) in the same manner as above. Recrystallization from CH_2Cl_2–hexane gave colorless needles (7.0 g, 86.1%), mp 77 °C. IR $\nu_{\max}^{\mathrm{KBr}}\,\mathrm{cm}^{-1}$: 2250 (CN), 1050 (S–O). ^{1}H-NMR ($CDCl_3$) δ: 2.34 (3H, s, CH_3), 2.88—2.45 (4H, m, CH_2CH_2), 3.62 (2H, AB q, $\Delta\nu = 11.7$ Hz, $J = 15.8$ Hz, CH_2CN), 7.13 (4H, s, ArH). *Anal.* Calcd for $C_{11}H_{13}NOS$: C, 63.74; H, 6.32; N, 6.76. Found: C, 63.99; H, 6.30; N, 6.79.

1-Cyanoisothiochroman (4a)——Trifluoroacetic anhydride (9.31 g, 44.3 mmol) was added to a solution of **3a** (5.71 g, 29.5 mmol) in CH_2Cl_2 (110 ml) with cooling in an ice-bath under a nitrogen atmosphere. The mixture was refluxed for 10 h and then concentrated under reduced pressure. The residual oil was chromatographed on silica gel using hexane–ethyl acetate (5 : 1) to give colorless crystals. Recrystallization from CH_2Cl_2–hexane gave colorless prisms (3.67 g, 70.9%), mp 67—68 °C (lit.[7] 63—64 °C). IR $\nu_{\max}^{\mathrm{KBr}}\,\mathrm{cm}^{-1}$: 2220 (CN). ^{1}H-NMR ($CDCl_3$) δ: 2.78—3.40 (4H, m, CH_2CH_2), 4.66 (1H, s, H-1), 7.22 (4H, br s, ArH). MS *m/z*: 175 (M^+).

1-Cyano-7-methylisothiochroman (4b)——In the same way as above, **3b** (6.35 g, 30.6 mmol) was cyclized with trifluoroacetic anhydride (9.64 g, 49.5 mmol). Recrystallization from ether–hexane gave pale yellow prisms (5.35 g, 92.3%), mp 59 °C. IR $\nu_{\max}^{\mathrm{KBr}}\,\mathrm{cm}^{-1}$: 2230 (CN). ^{1}H-NMR ($CDCl_3$) δ: 2.33 (3H, s, 7-CH_3), 2.78—3.39 (4H, m, CH_2CH_2), 4.64 (1H, s, H-1), 7.08 (3H, s, ArH). *Anal.* Calcd for $C_{11}H_{11}NS$: C, 69.80; H, 5.86; N, 7.40. Found: C, 70.06; H, 5.88; N, 7.39.

2-Alkyl-1-cyanoisothiochromanium Perchlorates (5)——A mixture of **4** (1.0 g), alkyl iodide (10 molar eq) and silver perchlorate (1 mol eq) in dry CH_2Cl_2 (14 ml) was stirred for a day at room temperature. The precipitate was filtered off and washed with acetone or acetonitrile. The washings and the filtrate were combined and concentrated under reduced pressure. Ether was added to the residue and the crystals were collected.

1-Cyano-2-methylisothiochromanium Perchlorate (**5a**): Recrystallization from acetone gave colorless prisms (94.1%), mp 210—211 °C (dec.). IR $\nu_{\max}^{\mathrm{KBr}}\,\mathrm{cm}^{-1}$: 2240 (CN), 1100 ($ClO_4^-$). ^{1}H-NMR ($CF_3CO_2H$) δ: 2.83 (3H, s, CH_3), 3.00—3.68 (3H, m, H-3,4), 4.30—4.55 (1H, m, H-3), 5.97 (1H, s, H-1), 7.40—7.86 (4H, m, ArH). *Anal.* Calcd for $C_{11}H_{12}ClNO_4S$: C, 45.60; H, 4.17; N, 4.83. Found: C, 45.45; H, 4.15; N, 4.77.

1-Cyano-2,7-dimethylisothiochromanium Perchlorate (**5b**): Recrystallization from acetonitrile–ether gave colorless prisms (78.9%), mp 153 °C. IR $\nu_{\max}^{\mathrm{KBr}}\,\mathrm{cm}^{-1}$: 2210 (CN), 1100 ($ClO_4^-$). ^{1}H-NMR ($CF_3CO_2H$) δ: 2.05 (3H, s, CH_3-7), 3.38 (3H, s, SCH_3), 2.57—3.30 (3H, m, H-3,4), 3.73—3.98 (1H, m, H-3), 5.48 (1H, s, H-1), 6.85—7.13 (3H, m, ArH). *Anal.* Calcd for $C_{12}H_{14}ClNO_4S$: C, 47.45; H, 4.65; N, 4.61. Found: C, 47.42; H, 4.69; N, 4.57.

1-Cyano-2-ethylisothiochromanium Perchlorate (**5c**): Recrystallization from acetone–ether gave colorless prisms (66.9%), mp 164—165 °C. IR $\nu_{\max}^{\mathrm{KBr}}\,\mathrm{cm}^{-1}$: 2240 (CN), 1100 ($ClO_4^-$). ^{1}H-NMR ($CF_3CO_2H$) δ: 1.63 (3H, t, $J = 6.8$ Hz, CH_3), 2.78—2.98 (6H, m, H-3,4 and SCH_2CH_3), 4.13—4.40 (1H, m, H-3), 6.03 (1H, s, H-1), 7.48—7.75 (4H, m, ArH). *Anal.* Calcd for $C_{12}H_{14}ClNO_4S$: C, 47.45; H, 4.65; N, 4.61. Found: C, 47.51; H, 4.76; N, 4.58.

These sulfonium salts were isomerized when their solutions in CF_3CO_2H were allowed to stand for a day at room temperature or heated for 1 h in a water-bath. The characteristic peaks of the newly formed isomers are at δ 3.06 (SCH_3) and 5.86 (H-1) for **5a**; 3.07 (SCH_3) and 5.85 (H-1) for **5b**; 1.69 (SCH_2CH_3), 5.94 (H-1) for **5c**.

2-Alkyl-1-cyano-3,4-dihydro-1*H*-2-thionianaphthalen-1-ides (6)——(a) Triethylamine (2 mol eq) was added to a cold solution of the sulfonium salt (**2**) (1.0 g) in ethanol (50 ml) with stirring under a nitrogen atmosphere. Stirring was continued for 8 h at room temperature. The mixture was poured into water (*ca.* 300 ml) and extracted with CH_2Cl_2. The extracts were washed with water and dried ($MgSO_4$). The solvent was evaporated off under reduced pressure. The residual solid was washed with ether and recrystallized from CH_2Cl_2–ether.

1-Cyano-2-methyl-3,4-dihydro-1*H*-2-thionianaphthalen-1-ide (**6a**): Colorless needles (99.1%), mp 131—132 °C (dec.). IR $\nu_{\max}^{\mathrm{KBr}}\,\mathrm{cm}^{-1}$: 2120 (CN). ^{1}H-NMR ($CDCl_3$) δ: 2.43 (3H, s, SCH_3), 2.78—3.53 (4H, m, H-3,4), 6.65—7.30 (4H, m, ArH). MS *m/z*: 189 (M^+). *Anal.* Calcd for $C_{11}H_{11}NS$: C, 69.80; H, 5.86; N, 7.40. Found: C, 69.55; H, 5.96; N, 7.24.

1-Cyano-2,7-dimethyl-3,4-dihydro-1*H*-2-thionianaphthalen-1-ide (**6b**): Colorless needles (62.6%), mp 154—155 °C (dec.). IR $\nu_{\max}^{\mathrm{KBr}}\,\mathrm{cm}^{-1}$: 2130 (CN). ^{1}H-NMR ($CDCl_3$) δ: 2.30 (3H, s, CH_3-7), 2.45 (3H, s, SCH_3), 2.83—3.50 (4H, m, H-3,4), 6.60—7.15 (4H, m, ArH). MS *m/z*: 203 (M^+). *Anal.* Calcd for $C_{12}H_{13}NS$: C, 70.90; H, 6.45; N, 6.89. Found: C, 70.67; H, 6.49; N, 6.87.

(b) The sulfonium salts **5** were treated with 2 mol eq of sodium hydride in tetrahydrofuran under a nitrogen atmosphere at an ice-bath temperature. The mixture was poured into water and extracted with CH_2Cl_2. Work-up as above afforded the ylides **6** in high yields.

Reaction of 6a with Perchloric Acid——Perchloric acid (70%) (23 mg) was added to a cold solution of **6a** (30 mg, 0.16 mmol) in acetone (6 ml). The mixture was stirred for 1 h at room temperature and then concentrated under reduced pressure. The crystalline solid was washed with ethanol and then ether and recrystallized from acetone to give 1-cyano-2-methylisothiochromanium perchlorate (**5a**) (38 mg, 84.8%). This sample was identical with an authentic specimen.

Thermal Reactions of the Ylides 6——A solution of **6** in an aprotic solvent was refluxed under a nitrogen atmosphere. The solvent was evaporated off and the residue was thin-layer-chromatographed on silica gel.

Reactions in Acetonitrile, DMF and Benzene: The product was separated by PTLC using hexane–ethyl acetate (5 : 1). Reaction conditions and products are listed in Table I.

1-Cyano-1-methylisothiochroman (**7**): Recrystallization from CH_2Cl_2–hexane gave colorless prisms, mp 52—53 °C. IR ν_{max}^{KBr} cm^{-1}: 2220 (CN). ^{1}H-NMR ($CDCl_3$) δ: 2.03 (3H, s, CH_3), 2.78—3.45 (4H, m, $CH_2 \times 2$), 7.10—7.58 (4H, m, ArH). MS *m/z*: 189 (M^+). *Anal.* Calcd for $C_{11}H_{11}NS$: C, 69.80; H, 5.86; N, 7.40. Found: C, 69.59; H, 5.78; N, 7.37. This was identical with an authentic sample prepared by the method of Böhme and Sitorus.[8]

Z-1,2-Dicyano-1,2-bis[*o*-(2-methylthioethyl)phenyl]ethene (**8-I**): Recrystallization from ether–hexane gave colorless prisms, mp 67.5—68.5 °C. UV λ_{max}^{EtOH} nm (ε): 208 (25000), 230 (sh, 14000), 280 (sh, 5330), 315 (7370). ^{1}H-NMR ($CDCl_3$) δ: 2.20 (6H, s, $SCH_3 \times 2$), 2.68—2.85 (4H, m, $SCH_2 \times 2$), 2.90—3.07 (4H, m, $ArCH_2 \times 2$), 6.84—7.32 (8H, m, ArH). ^{13}C-NMR ($CDCl_3$) δ: 15.9 (q, SCH_3), 33.1, 34.3 (t, CH_2S and CH_2Ar), 116.1 (s, CN), 126.9 (d), 128.6 (s), 129.3 (s), 129.9 (d), 130.1 (d), 130.8 (d), 139.1 (s). MS *m/z*: 378 (M^+). *Anal.* Calcd for $C_{22}H_{22}N_2S_2$: C, 69.80; H, 5.86; N, 7.40. Found: C, 69.55; H, 5.91; N, 7.35.

E-1,2-Dicyano-1,2-bis[*o*-(2-methylthioethyl)phenyl]ethene (**8-II**): Recrystallization from CH_2Cl_2–hexane gave colorless columns, mp 103—104 °C. UV λ_{max}^{EtOH} nm (ε): 209 (25900), 229 (sh, 12900), 303 (7060). ^{1}H-NMR ($CDCl_3$) δ: 2.09 (6H, s, $CH_3 \times 2$), 2.74—2.91 (4H, m, $CH_2S \times 2$), 3.03—3.20 (4H, m, $ArCH_2 \times 2$), 7.25—7.60 (8H, m, ArH). ^{13}C-NMR ($CDCl_3$) δ: 16.0 (q, SCH_3), 33.5, 35.1 (t, CH_2S and CH_2Ar), 115.2 (s, CN), 127.5 (d), 129.7 (d), 130.0 (s), 130.5 (d), 130.8 (s), 131.4 (d), 139.1 (s). MS *m/z*: 378 (M^+). *Anal.* Calcd for $C_{22}H_{22}N_2S_2$: C, 69.80; H, 5.86; N, 7.40. Found: C, 69.57; H, 5.79; N, 7.19.

Reactions in Toluene and Its Derivatives——Products and yields are shown in Table I. Products (**10a**—**c**) were recrystallized from CH_2Cl_2–hexane to give colorless prisms. 1-Benzyl-1-cyanoisothiochroman (**10a**), mp 133—134 °C. IR ν_{max}^{KBr} cm^{-1}: 2220 (CN). ^{1}H-NMR ($CDCl_3$) δ: 2.75—3.10 (4H, m, $CH_2 \times 2$), 3.49 (2H, AB q, $\Delta\nu = 20.0$ Hz, $J = 13.5$ Hz, $PhCH_2$), 7.10—7.50 (9H, m, ArH). MS *m/z*: 265 (M^+). *Anal.* Calcd for $C_{17}H_{15}NS$: C, 76.94; H, 5.70; N, 5.28. Found: C, 76.69; H, 5.69; N, 5.27. This was identical with an authentic sample prepared by the method of Böhme *et al.*[14] 1-Cyano-1-(*p*-methylbenzyl)isothiochroman (**10b**), mp 135 °C. IR ν_{max}^{KBr} cm^{-1}: 2220 (CN). ^{1}H-NMR ($CDCl_3$) δ: 2.32 (3H, s, CH_3), 2.75—3.18 (4H, m, $CH_2 \times 2$), 3.45 (2H, AB q, $\Delta\nu = 21.6$ Hz, $J = 13.5$ Hz, $MeC_6H_4CH_2$), 7.10—7.50 (8H, m, ArH). MS *m/z*: 279 (M^+). *Anal.* Calcd for $C_{18}H_{17}NS$: C, 77.38; H, 6.18; N, 5.01. Found: C, 77.58; H, 6.09; N, 5.06. 1-Cyano-1-(*p*-methoxybenzyl)isothiochroman (**10c**), mp 141 °C. IR ν_{max}^{KBr} cm^{-1}: 2220 (CN). ^{1}H-NMR ($CDCl_3$) δ: 2.78—3.18 (4H, m, $CH_2 \times 2$), 3.45 (2H, AB q, $\Delta\nu = 20.0$ Hz, $J = 13.5$ Hz, $MeOC_6H_4CH_2$), 3.80 (3H, s, OCH_3), 6.72—7.52 (8H, m, ArH). MS *m/z*: 295 (M^+). *Anal.* Calcd for $C_{18}H_{17}NOS$: C, 73.19; H, 5.80; N, 4.74. Found: C, 73.05; H, 5.81; N, 4.83.

Thermal Reaction of 6a with the Sulfonium Salt 5a——A solution of **6a** (100 mg, 0.53 mmol) and **5a** (3 mg) in dry dichloromethane (20 ml) was refluxed for 21 h under a nitrogen atmosphere. The solvent was evaporated off under reduced pressure. The residue was separated by preparative TLC on silica gel using hexane–ethyl acetate to give **8-I** (10 mg, 10%) and **8-II** (49 mg, 48%).

Dimerization Reaction of 6a with Tetracyanoethylene (TCNE)——A solution of **6a** (300 mg, 1.6 mmol) and TCNE (20 mg, 0.16 mmol) in dry dichloromethane (50 ml) was stirred at room temperature for 36 h under a nitrogen atmosphere. The solvent was removed under reduced pressure and the residue was separated in the same way as above. **8-I** (30 mg, 10%) and **8-II** (140 mg, 46.6%) were obtained.

Dimerization Reaction of 6a with 7,7,8,8-Tetracyanoquinodimethane (TCNQ)——A solution of **6a** (300 mg, 1.6 mmol) in dry dichloromethane (50 ml) was treated in the same way as above. **8-I** (39 mg, 13.0%) and **8-II** (120 mg, 40.0%) were obtained.

Photochemical Reaction of 8-II——A solution of **8-II** (100 mg, 0.26 mmol) in ethanol (100 ml) was exposed to sunlight for 3 h. The solvent was removed under reduced pressure to give a crystalline solid. Recrystallization from ethanol gave *E*-1,2-dicyano-1,2-bis[*o*-(2-methylsulfinylethyl)phenyl]ethene (**9**) as colorless prisms (20 mg, 18.4%), mp 169—170 °C. This sample was identical with an authentic sample prepared by oxidation of **8a** with MCPBA.

***E*-1,2-Dicyano-1,2-bis[*o*-(2-methylsulfinylethyl)phenyl]ethene (9)**——MCPBA (85% pure) (23 mg, 0.13 mmol) was added to a solution of **8-II** (80 mg, 0.13 mmol) in dry CH_2Cl_2 (20 ml) with stirring in an ice-bath and the reaction mixture was stirred for 1 h. Equimolar MCPBA was added to the mixture. Stirring was continued for 10 h and the mixture was treated with 5% $NaHCO_3$. The organic layer was dried ($MgSO_4$) and evaporated. The residual solid was recrystallized from ethanol to give colorless prisms (65 mg, 88.1%), mp 168—170 °C. IR ν_{max}^{KBr} cm^{-1}: 2215 (CN). ^{1}H-NMR ($CDCl_3$) δ: 2.62 (6H, s, $SCH_3 \times 2$), 2.80—3.60 (8H, m, $CH_2CH_2 \times 2$), 7.30—8.00 (8H, m, ArH). MS *m/z*: 410 (M^+). *Anal.* Calcd for $C_{22}H_{22}N_2O_2S_2$: C, 64.36; H, 5.40; N, 6.82. Found: C, 64.10; H, 5.57; N, 6.67.

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