m/e 212 (80, M^+), 195 (100); IR 2210 (C≡N), 1660 cm^{-1} (C=O).

Anal. Calcd for $C_{11}H_8N_4O$: C, 62.25; H, 3.80; N, 26.40. Found: C, 62.13; H, 3.75; N, 26.37.

Method B. To an ice-cooled solution of 0.7 g of Cl_2 in 40 mL of 0.2 N aqueous NaOH was added portionwise 0.5 g of **3a**. Stirring was continued for 1 h on cooling and for an additional 1 h at 50 °C. The resulting precipitates were filtered, washed with water and ethanol, and dried to give 0.2 g of white powder, which was identical (IR) with the above product (**6**). The same compound (1.2 g) was obtained from 2-phenylimidazole-4,5-dicarbonitrile[6] (2 g) with stirring at room temperature for 5 h in a mixture of 1 N aqueous NaOH (10 mL) and 30% aqueous H_2O_2 (2 mL).

General Procedure for Cyclization of 3 into 7. Amide **3a** (20 mmol) was stirred in 90 mL of 28% aqueous ammonia at room temperature for 3 h. Filtration and washing with water gave the product in almost quantitative yield. The reaction with aqueous NaOH also gave the same product, but was accompanied by some decomposition. 4-(Benzylideneamino)-3,5-diamino-2*H*-pyrrol-2-one (**7a**): mp 243–247 °C dec (from ethanol); IR 1748 cm^{-1} (C=O); ^1H NMR δ 8.87 (s, 1, =C**H**–), 7.46–7.52 and 7.92–8.02 (m, total 5, Ph), and broad peaks (N**H**) at 7.1 and 8.9; MS *m/e* 214 (30), 111 (92), 83 (100).

Anal. Calcd for $C_{11}H_{10}N_4O$: C, 61.67; H, 4.71; N, 26.16. Found: C, 61.64; H, 4.74; N, 25.89.

Similarly, amides **3b–g** were applied to the cyclization reaction to give 4-R^1R^2C=N– derivatives of 3,5-diamino-2*H*-pyrrol-2-one [compound number (R^1, R^2), % yield, decomposition point[22] (recrystallization solvent)]: **7b** (H, 4-$CH_3C_6H_4$), 97, 257–259 °C (MeOH); **7c** (H, 4-$CH_3OC_6H_4$), 94, ~230 °C (Me_2NCHO + CH_3CN); **7d** (H, 9-anthranyl), 86, ~205 °C (MeOH); **7e** (H, 4-$NO_2C_6C_6H_4$), 97, 238–242 °C (MeOH); **7f** (CH_3, 4-$NO_2C_6H_4$), 97, 250–255 °C (MeOH); **7g** (Ph, Ph), 94, 200–201 °C (CH_3CN). These compounds were identified by both consistent results of spectral properties and microanalyses.

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Registry No.—**4a,** 57443-97-7; **4b,** 57444-00-5; **5a,** 68568-24-1; **5b,** 68568-25-2; **6,** 68568-26-3; **7a,** 68568-27-4; **7b,** 68568-28-5; **7c,** 68568-29-6; **7d,** 68568-30-9; **7e,** 68568-31-0; **7f,** 68568-32-1; **7g,** 68568-33-2; benzaldehyde, 100-52-7; *p*-tolualdehyde, 104-87-0; *p*-anisaldehyde, 123-11-5; 9-anthracenecarboxaldehyde, 642-31-9; *p*-nitrobenzaldehyde, 555-16-8; 4′-nitroacetophenone, 100-19-6; benzophenone, 119-61-9; 2-phenylimidazole-4,5-dicarbonitrile, 50847-06-8.

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Reactions of Thiirene 1,1-Dioxides with α-Metalated Nitriles

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Reactions of thiirene 1,1-dioxides with α-metalated nitriles are described. 2,3-Dimethylthiirene 1,1-dioxide (**1a**) was found to act as an ambident electrophile to afford two types of sulfur-containing cyclic products, sulfolenes **3** and **7**, in moderate yields when the metalated nitriles have no α-hydrogen atom. The former (**3**) arose from nucleophilic attack of the aryl-substituted carbanions to the ring carbon of **1a**, and the latter (**7**) arose from the attack of an alkyl-substituted carbanion to the sulfur atom. When nitriles bear an α-hydrogen atom, acyclic products were obtained. On the other hand, 2,3-diphenylthiirene 1,1-dioxide suffered only one type of nucleophilic attack to the ring carbon atom. They gave sulfinate salts **9**, which can easily be converted to sulfolenes **10**, in good yields. The whole reactions are quite sensitive to the substituents of the thiirenes and nitriles.

Thiirenes are one of the 3-heterocyclopropenes which have been of great interest for many chemists, not only because of their highly strained structures but also because of their antiaromaticity.[1-3] While no thiirenes have been isolated, a few thiirene 1,1-dioxides have been prepared[4-6] and studied from both structural and theoretical points of view. The structure of the compounds was determined by X-ray crystallographic analysis,[7] and molecular orbital calculations showed weak conjugation between the ethylenic and sulfonyl groups.[1-3] However, chemical properties of thiirene 1,1-dioxides have not yet been well studied and only a few reactions have been reported on 2,3-diphenylthiirene 1,1-diox-

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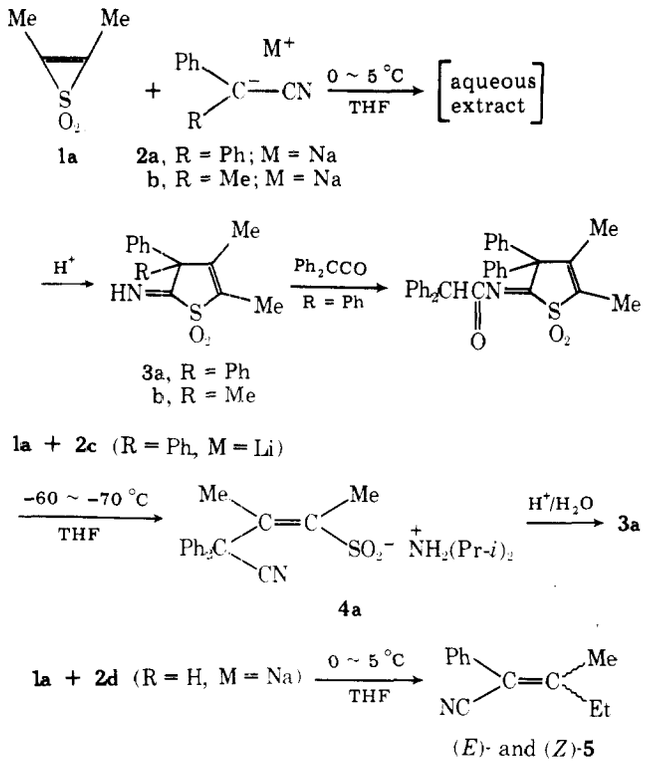
Scheme I



ide.[5,8-10] Furthermore, nothing is known for alkyl-substituted thiirene dioxides except for thermal decomposition and alkaline hydrolysis.[4-6]

In our preliminary report we found nucleophilic addition of α-metalated nitriles to 2,3-dimethylthiirene 1,1-dioxide.[11] We wish to report our further investigation on this reaction with 2,3-dimethyl- and 2,3-diphenylthiirene 1,1-dioxides and show their synthetic utility for the preparation of sulfur-containing heterocycles.

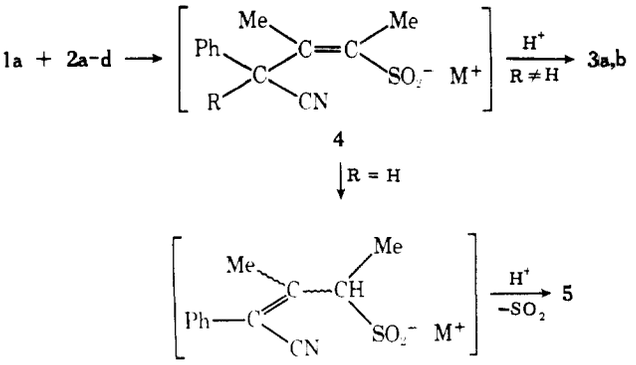
Results and Discussion

Reaction of 2,3-Dimethylthiirene 1,1-Dioxide (1a). The thiirene **1a** was allowed to react with α-sodiodiphenylacetonitrile (**2a**) and α-sodio-2-phenylpropionitrile (**2b**) in tetrahydrofuran at 0 ~ 5 °C (Scheme I). After standing for several hours at ambient temperature, removal of the solvent, and addition of water, only the unreacted nitriles were extracted with chloroform. After the aqueous layer was gradually acidified with dilute hydrochloric acid, the 5-imino-2,3-dimethyl-2-sulfolenes (**3a,b**) were isolated in 85 and 42% yields, respectively (based on the reacted nitriles). These results suggest the formation of water-soluble precursors of these sulfolenes.

On the other hand, the reaction with α-lithiodiphenylacetonitrile (**2c**) at −60 ~ −70 °C gave the sulfinate salt **4a** upon neutralization with hydrochloric acid. This salt was probably extracted with chloroform because of the use of lithium diisopropylamide as a base. Treatment of an aqueous solution of the salt **4a** with an equimolar amount of hydrochloric acid gave the sulfolene **3a** quantitatively. Thus, it is reasonable to assume that the precursors mentioned above are sodium sulfinates corresponding to **4a**, and hence there was no essential effect caused by the change of the counterion, M^+, or the reaction temperature.

It was rather striking that the imino compound **3a** separated out upon acidification in spite of the predictable instability of such imines under acidic conditions. The infrared spectrum of the sulfolene **3a** shows absorption bands at 3200 (NH), 1670 (C=N), and 1640 (C=C) cm^{-1}, as well as two absorptions at 1150 and 1280 cm^{-1} due to the symmetric and asymmetric

Scheme II



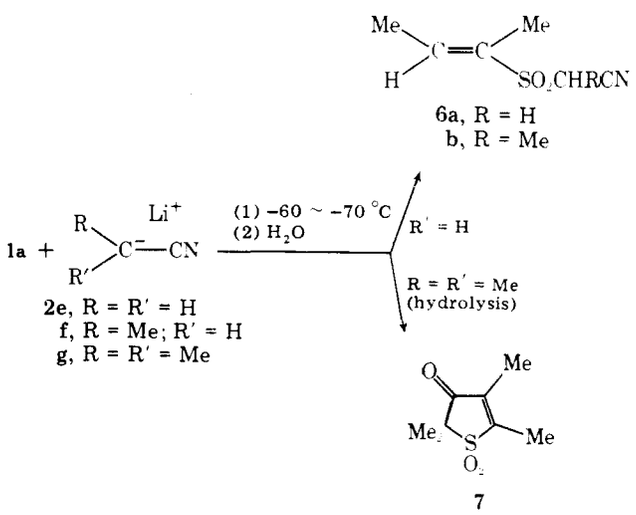
stretchings of the sulfonyl group. ^1H NMR (see Experimental Section) and ^{13}C NMR (vide infra) data also support the structure of **3**. The imino group of **3** was very sensitive to acidic hydrolysis and was easily acylated upon treatment with diphenylketene. Compound **4a** showed IR absorptions of the cyano (2240 cm^{-1}), the olefinic (1610 cm^{-1}), and the sulfinate groups (960 and 1010 cm^{-1}) along with several weak absorptions characteristic of ammonium salts in the region of 2400 ~ 2800 cm^{-1}.

However, the reaction of **1a** with α-sodiophenylacetonitrile (**2d**), which has a hydrogen atom at the α position of the cyano group, afforded a mixture of acrylonitrile derivatives (*E*)-**5** and (*Z*)-**5** (48:52) that are considered to be formed by the elimination of sulfur dioxide.

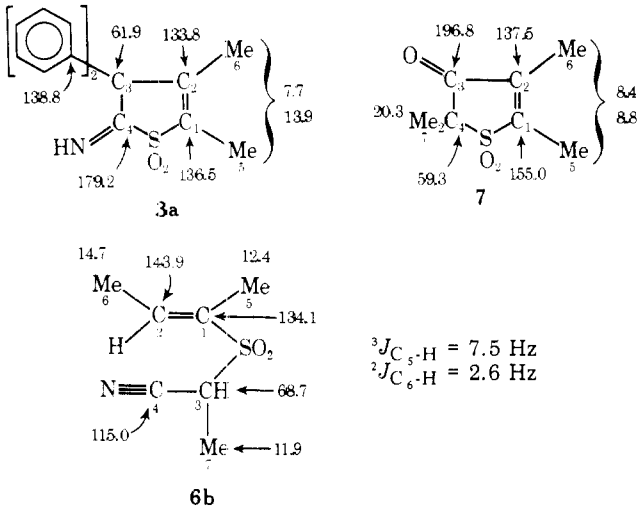
The above results indicated that the cyano carbanions **2a–d** generated from the phenyl-substituted acetonitriles nucleophilically attack the ring carbon of the thiirene **1a**. Thus, the formation of **3a,b** and **5** could be formulated as shown in Scheme II. Nucleophilic attack of the metalated nitriles **2a–d** on **1a** followed by ring opening may proceed via a sulfinate salt **4**. When **4** has no proton at the α position of the cyano group (R ≠ H), intramolecular cycloaddition of sulfinic acid, generated by acidification of **4**, to the carbon–nitrogen triple bond takes place to form the sulfolenes **3a,b**. The salt, which has an α-hydrogen atom (R = H), is subject to migration of the proton and elimination of sulfur dioxide, leading to **5**.

As described above, the reactivity of **1a** toward metalated nitriles differs according to the substituents of the nitriles. Furthermore, a completely different reaction manner was observed for the reactions with aliphatic nitriles. Reactions of **1a** with metalated nitriles **2e,f** gave acyclic vinyl sulfone derivatives **6a** and **6b** (Scheme III). ^1H NMR spectra show that olefins **6** are not mixtures of geometric isomers, and the

Scheme III



Scheme IV. ^{13}C NMR Chemical Shifts[a] of the Compounds 3a, 6b, and 7



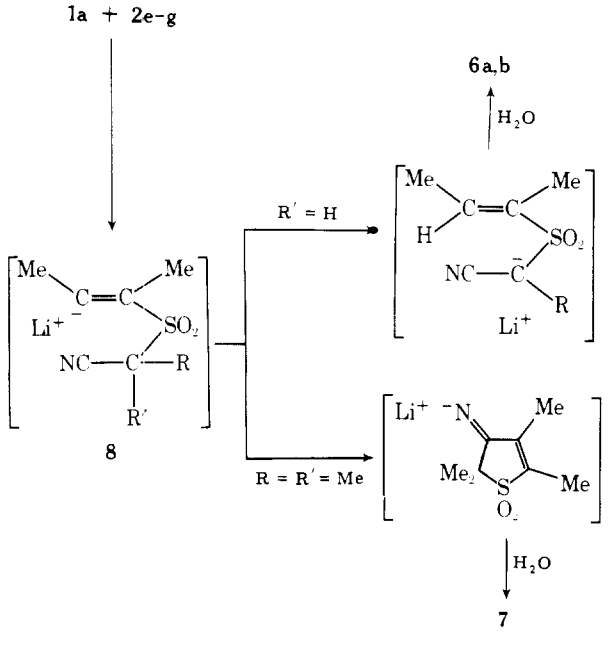
[a] In parts per million downfield from Me_4Si in $CDCl_3$ solutions.

cis-butene structure is supported by the coupling constant between C_5 and the olefinic proton ($^3J_{C_5\text{-}H}$) of **6b**; the value of 7.5 Hz is quite large for a *trans*-butene structure (see Scheme IV).[12]

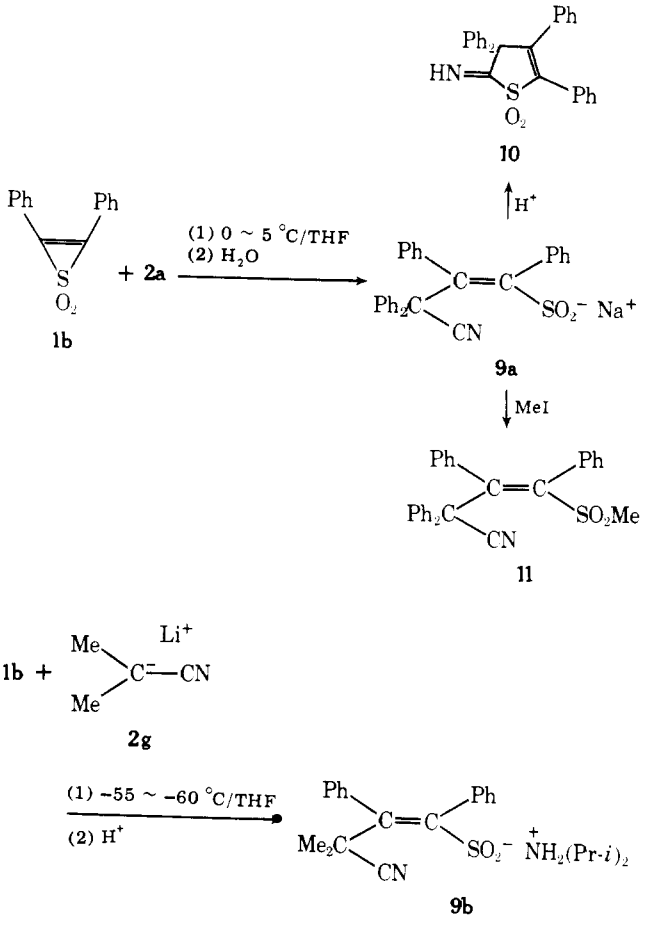
With dialkyl-substituted nitrile **2g**, the thiirene **1a** formed a cyclic compound, the sulfolene **7**. The 4-one structure of **7** was confirmed by UV and other spectral data. Comparison of ^{13}C NMR spectra of the sulfolenes **3a** and **7** is very informative. While the spectrum of **3a** seems to show normal chemical shifts of the vinyl carbons of α,β-unsaturated sulfones, a large low field shift of one of the vinyl carbons of **7** is consistent with that of α,β-unsaturated carbonyl groups.[13]

The products **6** and **7** are probably formed by the nucleophilic attack of **2e–g** to the sulfur atom of the thiirene **1a**. Thus, a remarkable contrast was observed with respect to the reactions initiated by nucleophilic attack of the phenyl-substituted nitriles on the ring carbon atom of **1a**. The formation of the compounds **6** and **7** is explained by invoking a vinyl carbanion intermediate **8** as shown in Scheme V. In this case,

Scheme V



Scheme VI



a hydrogen atom on the α carbon of the nitrile again changes the course of the reaction, causing intramolecular anion exchange that leads to **6**. When there is no α-hydrogen atom, intramolecular cycloaddition of the vinyl carbanion to the cyano group gives rise to an iminosulfolene derivative, which could easily be hydrolyzed to give **7** during aqueous workup and column chromatography.

These results revealed that dimethylthiirene 1,1-dioxide (**1a**) acts as an ambident electrophile according to the substituents of the metalated nitriles; the vinyl carbons were the electrophilic sites in the reaction with the α-metalated α-arylnitriles **2a–d,** but the sulfur atom was attacked by the anions from the α-metalated aliphatic nitriles **2e–g** that have no aryl groups at the α positions.

Reaction of 2,3-Diphenylthiirene 1,1-Dioxide (1b). It is interesting to know whether diaryl-substituted thiirene dioxide **1b** shows similar reactivity toward these carbanions. The reaction of the thiirene **1b** with α-sodiodiphenylacetonitrile (**2a**) gave a sulfinate salt **9a** in 64% yield when the reaction mixture was concentrated without acidification (Scheme VI). The compound **9a** corresponds to the salt **4** and was treated with an equimolar amount of hydrochloric acid to afford the sulfolene **10,** which corresponds to **3,** in 61% yield. The sodium salt **9a** was further confirmed by the reaction with methyl iodide, giving the vinyl sulfone **11**. Thus, with the carbanion **2a** the thiirene **1b** showed essentially the same type of reaction as that of the dialkyl-substituted thiirene **1a**.

On the other hand, the dialkyl-substituted carbanion **2g** did not change the attacking site, and again nucleophilic attack onto the ring carbon atom on the thiirene **1b** was observed. The reaction gave quantitatively the ammonium sulfinate **9b**, which derived from the use of lithium diisopropylamide for the preparation of the carbanion **2g**. This was also the case

with the formation of **4a**. So far, ambident electrophilic behavior was not found for the thiirene **1b**, which shows different properties from those of the thiirene **1a**.

Experimental Section

Melting points were determined with a Yamato MP-21 apparatus and were uncorrected. ^1H and ^{13}C NMR spectra were recorded with Jeol JNM-PMX-60 and JNM-FT-100 spectrometers in deuteriochloroform solutions unless otherwise noted. Infrared spectra were obtained on a Jasco IRA-1 spectrometer in a Nujol mull unless otherwise mentioned. Mass spectra were determined with a Hitachi RMU-6E spectrometer at an ionizing voltage of 70 eV.

2,3-Dimethylthiirene 1,1-dioxide (**1a**) and 2,3-diphenylthiirene 1,1-dioxide (**1b**) were prepared according to the literature.[5,6] Commercially available nitriles were used except for 2-phenylpropionitrile, which was prepared from the corresponding oxime by dehydration.[14,15] Liquid nitriles were distilled prior to use. Diphenylketene was obtained from diphenylacetyl chloride according to the known method.[16]

All reactions were carried out under a nitrogen atmosphere using tetrahydrofuran (THF) distilled from sodium metal. Metalated nitriles were prepared in two ways.

(A) Sodium hydride (50% in mineral oil) was washed with anhydrous *n*-hexane and dried in vacuo. After the reaction vessel was purged with nitrogen gas, a solution of a nitrile in THF was added and stirred at room temperature or at an elevated temperature if necessary.

(B) A solution of diisopropylamine in THF was added to a solution of *n*-butyllithium (15% in hexane) in THF at 0 ~ 5 °C and stirred at room temperature for 1 h. To the resulting lithium diisopropylamide (LDA) was added a solution of a nitrile in THF at −60 ~ −70 °C, and the mixture was stirred for 3 ~ 5 h at the same temperature.

Reaction of 2,3-Dimethylthiirene 1,1-Dioxide (1a) with α-Sodiodiphenylacetonitrile (2a). A mixture of 0.4 g (8.3 mmol) of sodium hydride and 1.6 g (8.3 mmol) of diphenylacetonitrile in 25 mL of THF was stirred at room temperature for 3 h. Then 1.0 g (8.5 mmol) of **1a** in 20 mL of THF was added dropwise to the solution at 0 ~ 5 °C, and the mixture was stirred at room temperature for another hour. The resulting reaction mixture was quenched (2 mL of H_2O), neutralized (dilute HCl), and concentrated under reduced pressure. The residue was extracted ($CHCl_3$–H_2O), and 0.65 g of the unreacted nitrile was recovered from the organic layer. The aqueous layer was gradually acidifed (dilute HCl), and the resulting milky turbidity was quickly extracted ($CHCl_3$). The extract was washed (H_2O), dried (Na_2SO_4), and concentrated in vacuo to give 1.4 g (85% based on the reacted nitrile) of 5-imino-2,3-dimethyl-4,4-diphenyl-2-sulfolene (**3a**). The compound **3a** was recrystallized from benzene to afford colorless needles: mp 162.5 ~ 164 °C dec; IR 3200 (NH), 1670 (C=N), 1640 (C=C), 1280 and 1150 (SO_2) cm^{-1}; UV (CH_3CN) 213.4 nm (log ε 4.15), 288.0 (1.91); ^1H NMR δ 1.78 (q, 3, J = 0.8 Hz, Me), 2.22 (q, 3, J = 0.8 Hz, Me), 7.1 ~ 7.6 (m, 11, NH and 2Ph); ^{13}C NMR data are given in Scheme IV; mass spectrum, m/e 311 (M^+), 247 ($M^+ - SO_2$).

Anal. Calcd for $C_{18}H_{17}NO_2S$: C, 69.42; H, 5.38; N, 4.39; S, 10.28. Found: C, 69.18; H, 5.52; N, 4.52; S, 10.25.

Reaction of 1a with α-Sodio-2-phenylpropionitrile (2b). A mixture of 0.41 g (8.5 mmol) of sodium hydride and 1.2 g (9.0 mmol) of 2-phenylpropionitrile in 25 mL of THF was stirred at 40 ~ 50 °C for 8 h to generate the salt **2b**. Then 1.0 g (8.5 mmol) of **1a** in 25 mL of THF was added dropwise to the solution at 0 ~ 5 °C. The mixture was stirred at the same temperature for 15 min and left overnight at room temperature. The reaction mixture was worked up according to the precedingly outlined procedure to give 0.57 g of the unreacted nitrile from the organic extract. The aqueous layer was acidified (dilute HCl), extracted ($CHCl_3$), washed (saturated $NaHCO_3$ solution and water), and dried (Na_2SO_4). Removal of the solvent under reduced pressure gave 500 mg (42% based on the reacted nitrile) of 5-imino-2,3,4-trimethyl-4-phenyl-2-sulfolene (**3b**), which was recrystallized from anhydrous ether as colorless needles: mp 113 ~ 114.5 °C dec; IR 3210 (NH), 1660 (C=N), 1640 (C=C), 1280 and 1125 (SO_2) cm^{-1}; ^1H NMR δ 1.73 (q, 3, J = 0.8 Hz, Me), 1.87 (s, 3, Me), 2.20 (q, 3, J = 0.8 Hz, Me), 7.36 (s, 5, Ph), 10.3–11.5 (broad, 1, NH); mass spectrum, m/e 135 ($M^+ - SO_2$).

Anal. Calcd for $C_{13}H_{15}NO_2S$: C, 62.61; H, 6.08; N, 5.62; S, 12.86. Found: C, 62.50; H, 6.15; N, 5.43; S, 12.64.

Reaction of 1a with α-Lithiodiphenylacetonitrile (2c). To a solution of the salt **2c** prepared from 6.0 mL (9.7 mmol) of butyllithium, 0.86 g (8.6 mmol) of diisopropylamine, 1.6 g (8.3 mmol) of diphenylacetonitrile, and 30 mL of THF was added 1.0 g (8.5 mmol) of **1a** in 25 mL of THF dropwise at −60 ~ −70 °C, and the mixture was stirred for 15 min. The mixture was allowed to stand overnight at room temperature and was quenched (3 mL of H_2O), neutralized (dilute HCl), concentrated, and extracted ($CHCl_3$–H_2O). The organic layer was dried (Na_2SO_4), and the solvent was removed under reduced pressure to provide 2.9 g (83% based on **1a**) of crude diisopropylammonium 3-cyano-1,2-dimethyl-3,3-diphenylpropenylsulfinate (**4a**) as a yellow solid: mp 99 °C dec; IR 2400 ~ 2800 (ammonium), 2240 (C≡N), 1610 (C=C), 1010 and 960 (SO_2^-) cm^{-1}; ^1H NMR δ 1.24 (d, 12, 4Me), 1.58 (s, 3, Me), 1.96 (s, 3, Me), 3.21 (septet, 2, 2CH), 7.39 (s, 10, 2Ph), 7.6 ~ 9.5 (broad, 2, H_2N^+).

The structure of the salt **4a** was further confirmed by the following cyclization to **3a**.

Cyclization of the Salt 4a to the Sulfolene 3a. To a solution of 1.0 g (2.4 mmol) of the salt **4a** in 25 mL of water was added 1 mL of 2 N HCl, and the mixture was stirred for 15 min to separate out a white precipitate. The mixture was extracted ($CHCl_3$), dried (Na_2SO_4), and concentrated to give 800 mg (quantitative) of the sulfolene **3a**.

Diphenylacetylation of the Sulfolene 3a. A mixture of 240 mg (0.77 mmol) of **3a** and 200 mg (1.2 mmol) of diphenylketene in 45 mL of anhydrous benzene was allowed to stand at room temperature for 10 days. Upon removal of the solvent and addition of a small amount of ether, 45 mg of the unreacted sulfolene was recovered. Filtration of **3a** and concentration of the mother liquor gave 100 mg (26%) of 5-(diphenylacetylimino)-2,3-dimethyl-4,4-diphenyl-2-sulfolene. Recrystallization of the compound from ether–hexane gave colorless prisms: mp 168 ~ 169 °C; IR 1710 (C=O), 1680 (C=N), 1300 and 1160 (SO_2) cm^{-1}; ^1H NMR δ 1.84 (s, 3, Me), 2.11 (s, 3, Me), 5.04 (s, 1, CH), 7.0 ~ 7.6 (m, 20, 4Ph); mass spectrum, m/e 441 ($M^+ - SO_2$), 247 ($M^+ - SO_2 - Ph_2CCO$).

Anal. Calcd for $C_{32}H_{27}NO_3S$: C, 76.00; H, 5.39; N, 2.77. Found: C, 75.86; H, 5.28; N, 2.70.

Reaction of 1a with α-Sodiophenylacetonitrile (2d). A mixture of 300 mg (6.3 mmol) of sodium hydride and 740 mg (6.3 mmol) of phenylacetonitrile in 25 mL of THF was stirred at 45 ~ 50 °C for 6 h. Upon cooling, 600 mg (0.51 mmol) of **1a** in 25 mL of THF was added dropwise to the solution at 0 ~ 5 °C. After standing overnight at room temperature and addition of 2 mL of water, the mixture was concentrated in vacuo. The residue was treated with 100 mL of chloroform and 40 mL of water and neutralized (dilute HCl). The organic extract was dried ($MgSO_4$), concentrated, and subjected to column chromatography (SiO_2–benzene–hexane), which gave 300 mg (40% based on the reacted nitrile) of a mixture of (*E*)- and (*Z*)-2-phenyl-3-methylpent-2-enenitrile (**5**; *E*/*Z* = 48:52 by ^1H NMR) and 300 mg of the unreacted nitrile. A mixture of the olefins **5** is a colorless liquid, and an analytical sample was obtained by preparative GLC: bp 100 ~ 109 °C (4 mm); IR (neat) 2230 (C≡N), 1620 (C=C) cm^{-1}; ^1H NMR δ 1.04 (t, (*E*)-Me), 1.19 (t, (*Z*)-Me), 1.86 (s, (*Z*)-Me), 2.16 (q, (*E*)-CH_2), 2.19 (s, (*E*)-Me), 2.57 (q, (*Z*)-CH_2), 7.23 (s, Ph); mass spectrum, m/e 171 (M^+).

Anal. Calcd for $C_{12}H_{13}N$: C, 84.17; H, 7.65; N, 8.18. Found: C, 83.81; H, 7.46; N, 8.34.

Reactions of 1a with α-Lithioacetonitrile (2e) and α-Lithiopropionitrile (2f). To a solution of the salt **2e** prepared from 5.8 mL (9.4 mmol) of butyllithium, 0.9 g (8.9 mmol) of diisopropylamine, 0.48 mL (9.2 mmol) of acetonitrile, and 25 mL of THF was added 1.0 g (8.5 mmol) of **1a** in 15 mL of THF dropwise, and the mixture was stirred at −60 ~ −70 °C for 30 min. The reaction mixture was worked up according to the same procedure as that for the reaction with **2c**. The organic extract was dried (Na_2SO_4) and concentrated in vacuo to afford 1.2 g of oily material. Column chromatographic treatment (SiO_2–benzene–hexane) of the crude oil gave 550 mg (41%) of *cis*-2-buten-2-yl cyanomethyl sulfone (**6a**). An analytically pure sample was obtained by preparative GLC as a colorless liquid: bp 105 ~ 110 °C (2–3 mm); IR (neat) 2250 (C≡N), 1640 (C=C), 1320 and 1120 (SO_2) cm^{-1}; ^1H NMR δ 1.96 (dq, 3, $J_{gem\text{-}H}$ = 7.0 Hz, J_{Me} = 1.2 Hz, Me), 2.10 (quintet, 3, $J_{vic\text{-}H}$ = J_{Me} = 1.2 Hz, Me), 3.96 (s, 2, CH_2), 7.04 (qq, $J_{gem\text{-}Me}$ = 7.0 Hz, $J_{vic\text{-}Me}$ = 1.2 Hz, CH=); mass spectrum, m/e 159 (M^+).

Anal. Calcd for $C_6H_9NO_2S$: C, 45.26; H, 5.71; N, 8.38. Found: C, 44.89; H, 5.75; N, 8.64.

Similarly, 950 mg of oily material was obtained from the reaction employing 0.86 g (8.6 mmol) of diisopropylamine, 6.3 mL (10.2 mmol) of *n*-butyllithium, 0.60 mL (8.5 mmol) of propionitrile, and 1.0 g (8.5 mmol) of **1a**. Treatment of the crude oil on a column (Al_2O_3) gave 600 mg of *cis*-2-buten-2-yl 1′-cyanoethyl sulfone (**6b**) from the fraction eluted with benzene–hexane and 300 mg of *cis*-2-buten-2-yl 1′-carbamoylethyl sulfone from the fraction eluted with chloroform. The latter compound was clearly produced by hydrolysis of **6b**. Thus, the combined yield of **6b** amounts to 60%.

6b: bp 85 ~ 90 °C (1 mm); IR (neat) 2250 (C≡N), 1645 (C=C), 1320 and 1120 (SO_2) cm^{-1}; ^1H NMR δ 1.76 (d, 3, J = 7.2 Hz, Me), 2.00 (dq, 3, J_{Me} = 1.2 Hz, $J_{gem\text{-}H}$ = 7.2 Hz, Me), 2.15 (quintet, 3, J_{Me} = $J_{vic\text{-}H}$ = 1.2 Hz, Me), 3.98 (q, 1, J = 7.2 Hz, CH), 7.10 (qq, 1, $J_{gem\text{-}Me}$ = 7.2 Hz, $J_{vic\text{-}Me}$ = 1.2 Hz, CH=); mass spectrum, *m/e* 173 (M^+).

Anal. Calcd for $C_7H_{11}NO_2S$: C, 48.53; H, 6.41; N, 8.09; S, 18.51. Found: C, 48.27; H, 6.35; N, 8.45; S, 18.13.

cis-2-Buten-2-yl 1'-carbamoylethyl sulfone: mp 108 ~ 109.5 °C (colorless plates from benzene); IR 3440, 3200 ~ 3300 (NH_2), 1680 (C=C), 1290 and 1120 (SO_2) cm^{-1}; ^1H NMR δ 1.53 (d, 3, J = 7.2 Hz, Me), 1.90 (dq, 3, J_{Me} = 1.2 Hz, $J_{gem\text{-}H}$ = 7.0 Hz, Me), 2.04 (quintet, 3, J_{Me} = $J_{vic\text{-}H}$ = 1.2 Hz, Me), 3.87 (q, 1, J_{Me} = 7.2 Hz, CH), 5.7 ~ 7.2 (broad, 2, NH_2), 6.85 (qq, 1, $J_{gem\text{-}Me}$ = $J_{vic\text{-}Me}$ = 1.2 Hz, CH=); mass spectrum, *m/e* 191 (M^+).

Anal. Calcd for $C_7H_{13}NO_3S$: C, 43.95; H, 6.86; N, 7.32. Found: C, 44.06; H, 6.89; N, 7.32.

Reaction of 1a with α-Lithioisobutyronitrile (2g). A solution of 1.0 g (8.5 mmol) of **1a** in 25 mL of THF was added slowly at −55 ~ −60 °C to a solution of the salt **2g** prepared from 0.88 g (8.7 mmol) of diisopropylamine, 6.3 mL (10.1 mmol) of *n*-butyllithium, 600 mg (8.7 mmol) of isobutyronitrile, and 35 mL of THF. The mixture was stirred for 2 h at −60 °C and for 1.5 h at room temperature. Similar treatment to that for the reaction with **2c** gave 800 mg of an oily product which was subjected to column chromatography (SiO_2–benzene–hexane) to afford 530 mg (33%) of 2,3,5,5-tetramethyl-2-sulfolen-4-one (**7**). Compound **7** was recrystallized from ether–hexane to give colorless prisms: mp 84 ~ 85 °C; IR 1710 (C=O), 1640 (C=C), 1290 and 1100 (SO_2) cm^{-1}; UV (MeOH) 236.5 nm (log ϵ 4.09), 327.0 (1.40); ^1H NMR δ 1.48 (s, 6, 2Me), 1.95 (q, 3, J = 1.2 Hz, Me), 2.30 (q, 3, J = 1.2 Hz, Me); ^{13}C NMR data are given in Scheme IV; mass spectrum, *m/e* 188 (M^+).

Anal. Calcd for $C_8H_{12}O_3S$: C, 51.03; H, 6.44; S, 17.03. Found: C, 51.15; H, 6.28; S, 16.92.

Reaction of 2,3-Diphenylthiirene 1,1-Dioxide (1b) with 2a. A solution of 1.0 g (4.1 mmol) of **1b** in 25 mL of THF was added dropwise at 0 ~ 5 °C to a solution of the salt **2a** prepared from 210 mg (4.4 mmol) of sodium hydride and 810 mg (4.2 mmol) of diphenylacetonitrile in 15 mL of THF. The mixture was allowed to stand at room temperature for 2 days. Then the reaction mixture was quenched (2 mL of H_2O) and neutralized (dilute HCl). The solvent was removed, and the residue was washed with small portions of water and chloroform to give 1.2 g (64%) of sodium 3-cyano-1,2,3,3-tetraphenylpropenylsulfinate (**9a**), which was recrystallized from THF to give colorless needles: mp 245 °C dec; IR 2240 (C≡N), 1030 and 980 (SO_2^-) cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 6.7 ~ 7.9 (aromatic protons).

Anal. Calcd for $C_{28}H_{20}NNaO_2S$: C, 73.50; H, 4.41; N, 3.06; S, 7.01. Found: C, 73.21; H, 4.18; N, 2.96; S, 6.69.

Methylation of the Salt 9a. In 15 mL of ethanol, 600 mg (1.4 mmol) of the salt **9a** and 0.5 mL (8.0 mmol) of methyl iodide were dissolved and heated at 45 ~ 50 °C for 3 days. After removal of ethanol, the resulting material was treated with a small amount of water, extracted ($CHCl_3$), and dried (Na_2SO_4). Upon removal of the solvent, 400 mg (68%) of 3-cyano-1,2,3,3-tetraphenylpropenyl methyl sulfone (**11**) was obtained. An analytical sample was purified by column chromatography (SiO_2–benzene–hexane) and recrystallization (colorless powder from ether–hexane): mp 60.5 ~ 62.5 °C; IR 2240 (C≡N), 1320 and 1140 (SO_2) cm^{-1}; ^1H NMR δ 3.47 (s, 3, Me), 6.7 ~ 7.8 (m, 20, 4Ph); mass spectrum, *m/e* 449 (M^+).

Anal. Calcd for $C_{29}H_{23}NO_2S$: C, 77.47; H, 5.17; N, 3.12. Found: C, 77.43; H, 5.29; N, 2.98.

Acidic Treatment of the Salt 9a. To a solution of 0.50 g (1.1 mmol) of the sulfinate **9a** in 10 mL of THF was added 0.34 mL of 3 N HCl, and the solution became slightly acidic. Upon removal of the solvent under reduced pressure, the residue was extracted ($CHCl_3$–H_2O). The organic extract was dried (Na_2SO_4) and concentrated to give 290 mg (61%) of 5-imino-2,3,4,4-tetraphenyl-2-sulfolene (**10**). Recrystallization of the compound from ether–hexane gave colorless needles: mp 82 °C dec; IR 3200 (NH), 1660 (C=N), 1305 and 1140 (SO_2) cm^{-1}; ^1H NMR δ 6.8 ~ 7.6 (NH and 4Ph); mass spectrum, *m/e* 419 ($M^+ - O$), 371 ($M^+ - SO_2$). The sulfolene **10** could not be made pure enough for satisfactory elemental analysis, probably because of the imino group which is sensitive to hydrolysis.

Reaction of 1b with α-Lithioisobutyronitrile (2g). A solution of **1b** (1.0 g, 4.1 mmol) in 17.5 mL of THF was added slowly at −50 ~ −60 °C to a solution of the salt **2g** prepared from 0.44 g (4.3 mmol) of diisopropylamine, 3.1 mL (5.0 mmol) of *n*-butyllithium, and 0.39 mL (4.4 mmol) of isobutyronitrile in 20 mL of THF. The mixture was stirred for 30 min at the same temperature. After standing overnight at room temperature, the same treatment as was done for the reaction of **1a** with **2c** afforded 1.7 g (100%) of crude diisopropylammonium 3-cyano-3-methyl-1,2-diphenylbut-1-en-1-ylsulfinate (**9b**) as a yellow solid. The compound **9b** was recrystallized from THF to give colorless prisms: mp 182 °C dec; IR 2500 ~ 3000 (ammonium), 2240 (C≡N), 1040 and 980 (SO_2^-) cm^{-1}; ^1H NMR δ 1.14 (d, 12, 4Me), 1.67 (s, 6, 2Me), 3.15 (septet, 2, CH), 6.8 ~ 7.7 (m, 10, 2Ph), 7.7 ~ 9.0 (broad, 2, NH_2). This salt could not be satisfactorily purified for elemental analysis mainly because of its hygroscopic property, and hence the following in situ methylation of **9b** was carried out.

Methylation of the Salt 9b. A THF solution containing the sulfinate **9b** was prepared from 0.56 g (5.5 mmol) of diisopropylamine, 4.0 mL (6.4 mmol) of *n*-butyllithium in 15 mL of THF, 0.50 mL (6.2 mmol) of isobutyronitrile in 5 mL of THF, and 1.0 g (4.1 mmol) of **1b** by the same procedure as shown in the preceding experiment. To the solution was added 1.1 mL (17.7 mmol) of methyl iodide, and the mixture was stirred at room temperature for 10 h and under reflux for 2.5 h. The reaction mixture was concentrated and extracted with ether–water. The organic extract was dried (Na_2SO_4), and the solvent was removed to give 600 mg of red-brown oil, from which 60 mg of 3-cyano-3-methyl-1,2-diphenylbut-1-en-1-yl methyl sulfone precipitated upon addition of ether. The mother liquor was chromatographed (SiO_2–$CHCl_3$) to give 300 mg of the same sulfone (total yield 27%), which was recrystallized from benzene to afford yellow needles: mp 261.5 ~ 263.5 °C; IR 2240 (C≡N), 1300 and 1140 (SO_2) cm^{-1}; ^1H NMR δ 1.36 (s, 6, 2Me), 2.43 (s, 3, Me), 7.2 ~ 7.4 (m, 10, 2Ph); mass spectrum, *m/e* 325 (M^+).

Anal. Calcd for $C_{19}H_{19}O_2S$: C, 70.12; H, 5.90; N, 4.30; S, 9.85. Found: C, 70.28; H, 5.90; N, 4.30; S, 9.83.

Registry No.—**1a**, 30646-57-2; **1b**, 5162-99-2; **2a**, 53847-23-7; **2b**, 34651-34-8; **2c**, 66785-30-6; **2d**, 26388-11-4; **2e**, 55440-71-6; **2f**, 59263-57-9; **2g**, 55440-70-5; **3a**, 67096-86-0; **3b**, 68707-45-9; **4a**, 68707-47-1; (*E*)-**5**, 68707-48-2; (*Z*)-**5**, 68707-49-3; **6a**, 68707-50-6; **6b**, 68707-51-7; **7**, 67096-87-1; **9a**, 68707-52-8; **9b**, 68707-54-0; **10**, 68707-55-1; **11**, 68707-56-2; 5-(diphenylacetylimino)-2,3-dimethyl-4,4-diphenyl-2-sulfolene, 68707-57-3; *cis*-2-buten-2-yl 1'-carbamoylethyl sulfone, 68707-58-4; 3-cyano-3-methyl-1,2-diphenylbut-1-en-1-yl methyl sulfone, 68707-59-5; diphenylketene, 525-06-4.

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