2,4,8,10-Tetra-*tert*-butyl-12*H*-dibenzo[*d*,*g*][1,3,2]dioxasilocin (5f). To 150 mL of dry tetrahydrofuran at 0 °C was added dropwise a solution of 42.46 g (0.10 mol) of **4a** and 20.24 g (0.20 mol) of triethylamine in 100 mL of tetrahydrofuran, and simultaneously was introduced 30.3 g (0.30 mol) of **2d** through a gas disparaging tube. The reaction mixture was stirred 3 h at room temperature and then the suspension of triethylamine hydrochloride was removed by filtration. The solvent was removed in vacuo and the residue was recrystallized from heptane to give 25.9 g (57%) of a white solid: mp 189–192 °C; MS: m/z 452 ($M^{+}\cdot$), 437 ($M^+ - 15$), 57 ($C_4H_9^+$).

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Registry No. 1, 6390-69-8; **2a**, 75-54-7; **2b**, 75-78-5; **2c**, 1631-84-1; **2d**, 4109-96-0; **3a**, 88946-07-0; **3b**, 88946-08-1; **4a**, 14362-12-0; **4b**, 35958-30-6; **5a**, 88946-09-2; **5b**, 88946-10-5; **5c**, 88946-11-6; **5d**, 88946-12-7; **5e**, 88946-13-8; **5f**, 88946-14-9.

Cycloaddition Reactions across the Carbon–Carbon Double Bond of Thiirene 1,1-Dioxide

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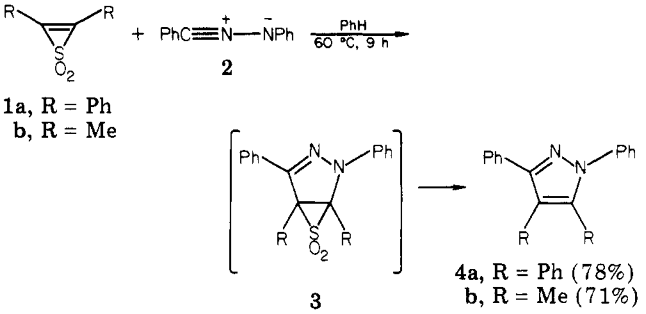
Chemical properties of thiirenes have been of great interest because of their highly strained structures and antiaromaticity.[1] We previously reported a novel ring-enlargement reaction of the thiirene 1,1-dioxides with α-metalated nitriles.[2] While the dioxides readily undergo ring-opening reactions with a variety of nucleophiles,[3-5a] their cycloaddition reactions have been little studied except for the reactions with enamines[6] and a few other reagents.[5,7]

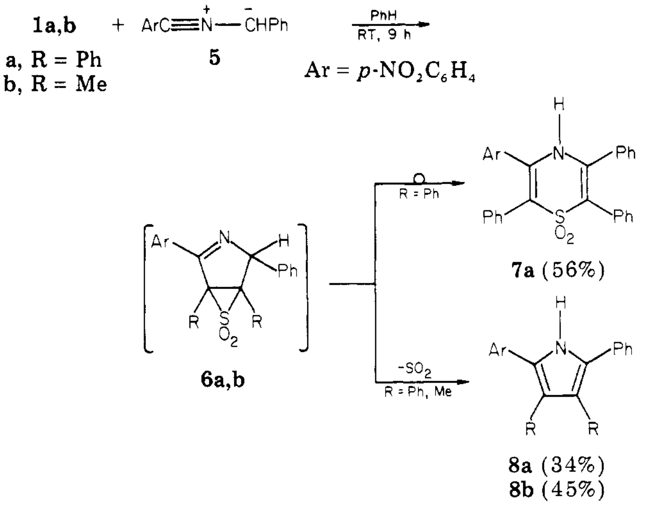
Here we report the cycloaddition reactions of the dioxides with enophiles such as 1,3-dipoles and a dienamine.

2,3-Diphenyl- and 2,3-dimethylthiirene dioxides (**1a** and **1b**) were allowed to react with benzonitrilium *N*-phenylimide (**2**), generated in situ from *N*-phenylbenzohydrazonoyl chloride and triethylamine, at 60 °C in benzene to give the pyrazole derivatives **4a** and **4b** in good yields.



The pyrazoles 4 are probably formed via the cycloadducts **3**, which eliminated sulfur dioxide. Ready extrusion of sulfur dioxide from an episulfone is well-known; a similar type of reaction was also observed for the formation of a pyrazole from **1a** and diazomethane.[8] The reaction at room temperature showed very slow conversion to the pyrazole **4**, and again the episulfone **3** could not be detected. Formation of the pyrazole **4** by the 1,3-cycloaddition of **2** to the acetylene derived from **1** is excluded by the following evidence: (a) decomposition of the thiirene dioxides into acetylenes was slow under the reaction conditions and (b) the adduct **4a** was obtained only in 3% yield even when diphenylacetylene was reacted with **2** in boiling benzene for 6 h.[9]

The thiirene dioxide **1a** gave two products when treated with the in situ generated nitrile ylide **5** in benzene at room temperature. The major product was determined to be 3-(*p*-nitrophenyl)-2,5,6-triphenyl-1,4-thiazine 1,1-dioxide (**7a**); the minor product was 2-(*p*-nitrophenyl)-3,4,5-triphenylpyrrole (**8a**). The NMR spectrum of the thiazine **7a** is featured by a broad singlet at δ 8.55 (one proton) which disappears upon addition of D_2O.[10]



The formation of the thiazine **7a** is explained by rearrangement of the 1:1 cycloadduct **6a**; elimination of sulfur dioxide from **6a** would give rise to the pyrrole **8a**. The rearrangment process might have been catalyzed by proton abstraction by triethylamine employed for generation of the ylide **5**. Similar ring expansion was reported for the 1:1 cycloadduct of **1a** and azide ion, which afforded a 1,3,4,5-thiatriazine 1,1-dioxide derivative along with a triazole derivative formed by SO_2 extrusion.[11,12]

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(10) Although the location of the Ar group could not be determined absolutely only by the spectral data, the assignments are readily understood by the chemical behavior of the thiirene 1 in the preceding reaction or in the reaction with azide ion (see the note 11).

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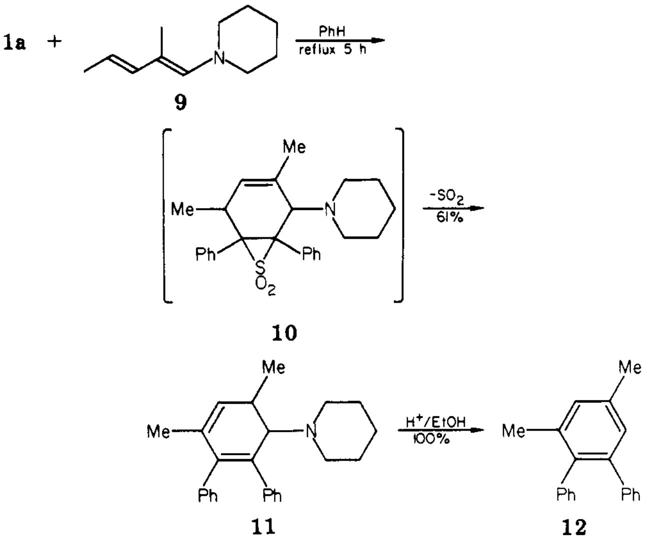
When 2,3-dimethylthiirene 1,1-dioxide (**1b**) was employed in the reaction with the ylide **5**, the corresponding pyrrole **8b** was obtained in 45% yield along with a considerable amount of the unreacted **1b**. Thus the alkyl-substituted thiirene **1b** seems to be a less reactive dipolarophile than the aryl analogue **1a**. The thiazine derivative was not formed, probably because of lower acidity of the proton of the cycloadduct intermediate and instability of the episulfone ring.

In contrast to the 1,3-dipoles mentioned above, benzonitrile oxide did not react with the thiirene dioxide 1 in boiling benzene.

The electron-rich diene, 1-piperidino-2-methyl-1,3-pentadiene (**9**), reacted with the thiirene **1a** in boiling benzene to afford 61% of the dihydrobenzene derivative 11. The 1,3-diene structure was supported by the NMR spectrum which was characterized by a doublet at δ 3.75 assignable to the methine proton adjacent to the piperidino nitrogen. The dihydrobenzene **11** was easily deaminated to the benzene derivative **12** when heated in refluxing EtOH for 3 h in the presence of hydrochloric acid.



It is rational to consider that the dihydrobenzene **11** is formed via the bicyclic episulfone **10** accompanied by sulfur dioxide extrusion. In the case of the 2,3-dimethyl analogue **1b**, only a small amount of the corresponding benzene derivative was obtained.

Experimental Section

Melting points were determined with a Yamato MP-21 apparatus. NMR spectra were recorded with a JEOL JNM-PMX 60 spectrometer in $CDCl_3$ solutions with tetramethylsilane as an internal standard unless otherwise noted. IR spectra were taken on a JASCO IR-A spectrometer in Nujol mulls. Mass spectra were obtained with a Hitachi RMU-6E spectrometer at an ionizing voltage of 70 eV. All the reactions were carried out under a nitrogen atmosphere with dry benzene as solvent.

Materials. 2,3-Diphenylthiirene 1,1-dioxide (**1a**),[13] 2,3-dimethylthiirene 1,1-dioxide (**1b**),[14] and 1-piperidino-2-methyl-1,3-pentadiene (**9**)[15] were prepared by known methods. Benzonitrilium *N*-phenylimide (**2**), *p*-nitrophenylbenzonitrile benzylide (**5**), and benzonitrile oxide were prepared by dehydrochlorination of *N*-phenylbenzohydrazonoyl chloride, *N*-benzyl-*p*-nitrobenzimidoyl chloride, and benzohydroximoyl chloride, respectively, according to the literature.[9,16,17]

Reactions of the Thiirene Dioxides 1a,b with the Nitrile Imine 2. To a solution of **1a** (1.0 g, 4.1 mmol) and *N*-phenylbenzohydrazonoyl chloride (1.9 g, 8.3 mmol) in benzene (25 mL) was added dropwise triethylamine (1.25 g, 12.4 mmol) at room temperature. After being stirred at 60 °C for 9 h, the reaction mixture was washed with water and the organic layer was dried (Na_2SO_4). The solvent was removed under reduced pressure to give 1.4 g (78%) of 1,3,4,5-tetraphenylpyrazole (**4a**) as a colorless solid upon addition of Et_2O to the residue: mp 217–218 °C (colorless prisms from CH_3CN); IR 1590 cm^{-1} (C=C); NMR δ 6.9–7.7 (4 Ph); MS *m/e* 372 (M^+).

Anal. Calcd for $C_{27}H_{20}N_2$: C, 87.10; H, 5.38; N, 7.53. Found: C, 86.86; H, 5.22; N, 7.73.

Similarly, 0.74 g (71%) of 1,3-diphenyl-4,5-dimethylpyrazole (**4b**) was obtained from 0.5 g (4.2 mmol) of **1b**, 1.95 g (8.5 mmol) of the hydrazonoyl chloride, and 1.28 g (12.7 mmol) of triethylamine. The pyrazole **4b** was isolated by column chromatography (SiO_2–benzene/hexane) and recrystallized from hexane to give colorless prisms: mp 89–90 °C; IR 1600 cm^{-1} (C=C); NMR δ 2.20 (s, 3 H, Me), 2.23 (s, 3 H, Me), 7.1–7.8 (m, 10 H, 2 Ph); MS, *m/e* 248 (M^+).

Anal. Calcd for $C_{17}H_{16}N_2$: C, 82.26; H, 6.45; N, 11.29. Found: C, 82.24; H, 6.24; N, 11.35.

Reaction of the Thiirene 1,1-Dioxides 1a,b with the Nitrile Ylide 5. To a solution of **1a** (1.0 g, 4.1 mmol) and *N*-benzyl-*p*-nitrobenzimidoyl chloride (1.7 g, 6.2 mmol) in benzene (30 mL) was added dropwise triethylamine (0.99 g, 9.8 mL) at room temperature, and the mixture was stirred for 9 h. The reaction mixture was concentrated and extracted ($CHCl_3$–H_2O). The organic layer was dried (Na_2SO_4) and concentrated to give 1.1 g (56%) of 2,3,6-triphenyl-5-(*p*-nitrophenyl)-1,4-thiazine 1,1-dioxide (**7a**) as a pale yellow solid upon addition of benzene. The mother liquor was concentrated and chromatographed on a silica gel column to give 0.57 g (34%) of 2,3,4-triphenyl-5-(*p*-nitrophenyl)pyrrole (**8a**; eluted with benzene/hexane).

The thiazine **7a** was recrystallized from EtOH to give colorless needles: mp 252 °C dec; IR 3240 (NH), 1630 (C=C), 1250, and 1130 cm^{-1} (SO_2); NMR (CD_3CN) δ 7.2–7.5 (m, 15 H, 3 Ph), 7.7–8.2 (dd, 4 H, p-$NO_2C_6H_4$), 8.4–8.7 (br, 1 H, D_2O exchangeable, NH); MS, *m/e* 480 (M^+).

Anal. Calcd for $C_{28}H_{20}N_2O_4S$: C, 69.98; H, 4.20; N, 5.83. Found: C, 69.54; H, 4.06; N, 5.85.

The pyrrole **8a** was recrystallized from EtOH to give red needles: mp 253–254 °C; IR 3450 (NH), 1590 cm^{-1} (C=C); NMR (Me_2SO-d_6) δ 6.9–7.7 (m, 15 H, 3 Ph), 7.5–8.2 (dd, 4 H, p-$NO_2C_6H_4$), 11.5–11.8 (br s, 1 H, exchangeable with D_2O, NH); MS, *m/e* 416 (M^+).

Anal. Calcd for $C_{28}H_{20}N_2O_2$: C, 80.77; H, 4.81; N, 6.73. Found: C, 80.48; H, 4.64; N, 6.54.

Similarly, the thiirene dioxide **1b** (0.85 g, 7.2 mmol) was treated with the chloride (2.98 g, 10.9 mmol) and triethylamine (1.65 g, 16.3 mmol) at room temperature for 9 h to afford 1.1 g (45%) of 2-phenyl-3,4-dimethyl-5-(*p*-nitrophenyl)pyrrole (**8b**), which was isolated by column chromatography (SiO_2–benzene/hexane) and recrystallized from EtOH to give red needles: mp 170–171 °C; IR 3420 (NH), 1580 cm^{-1} (C=C); NMR δ 2.23 (s, 3 H, Me), 2.30 (s, 3 H, Me), 7.2–8.4 (m, 10 H, aromatic protons and NH); MS, *m/e* 292 (M^+).

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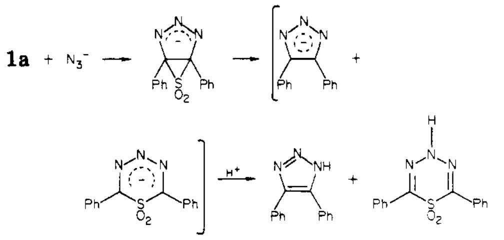
(11) The reaction path is elucidated as follows (see ref 7).



(12) The same type of ring expansion is also observed for the 1:1 cycloadduct of a cyclopropenone and a diazomethane, which rearranged into a dihydropyridazine derivative; see, for example: Aue, D. H.; Lorens, R. B.; Helwig, G. S. *J. Org. Chem.* **1979**, *44*, 1202.

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Anal. Calcd for $C_{18}H_{16}N_2O_2$: C, 73.97; H, 5.48; N, 9.59. Found: C, 73.67; H, 5.37; N, 9.55.

Reactions of the Thiirene Dioxides 1a,b with the Dienamine 9. To a solution of **1a** (1.0 g, 4.1 mmol) in benzene (30 mL) was added **9** (0.70 g, 4.1 mmol) at room temperature, and the mixture was stirred at reflux for 5 h. The reaction mixture was concentrated to give 0.85 g (61%) of 1,2-diphenyl-3,5-dimethyl-6-piperidino-1,3-cyclohexadiene (**11**) as a colorless solid upon addition of MeOH: mp 83–84 °C (colorless needles from EtOH); IR 1600 cm^{-1} (C=C); NMR δ 1.07 (d, 3 H, J = 7.6 Hz, Me), 1.3–1.8 (br m, 6 H, 3 CH_2), 1.84 (dd, 3 H, J = 1.6 and 1.6 Hz, Me), 2.1–3.3 (br m, 5 H, 2NCH_2 and CH), 3.75 (d, 1 H, J = 4.8 Hz, NCH), 5.68 (dq, 1 H, J = 4.4 and 1.6 Hz, =CH), 6.7–7.4 (m, 10 H, 2 Ph); MS, m/e 343 (M^+).

Anal. Calcd for $C_{25}H_{29}N$: C, 87.46; H, 8.45; N, 4.08. Found: C, 87.16; H, 8.40; N, 4.05.

Compounds **1b** (1.0 g, 8.5 mmol) and **9** (1.4 g, 8.2 mmol) were allowed to react in refluxing benzene for 11 h to give 12% (determined by GLC) of 1,2,3,5-tetramethylbenzene, whose IR and NMR spectra were in good agreement with those of an authentic sample.

Acidic Treatment of the Dihydrobenzene 11. A solution of **11** (0.4 g, 1.2 mmol) and 2 N HCl (6 mL) in EtOH (10 mL) was refluxed for 3 h. The reaction mixture was neutralized and extracted (Et_2O). The organic extract was dried (Na_2SO_4) and distilled to give 0.26 g (100%) of 3,5-dimethyl-1,2-diphenylbenzene (**12**): bp 93–97 °C (2 mmHg) by pot distillation; NMR (CCl_4) δ 2.10 (s, 3 H, Me), 2.37 (s, 3 H, Me), 6.9–7.3 (m, 12 H, aromatic protons); MS, m/e 258 (M^+).

Anal. Calcd for $C_{20}H_{18}$: C, 93.02; H, 6.98. Found: C, 92.84; H, 7.21.

Registry No. **1a**, 5162-99-2; **1b**, 30646-57-2; **2**, 15409-32-2; **4a**, 7189-13-1; **4b**, 7189-14-2; **5**, 73935-66-7; **7a**, 73935-71-4; **8a**, 73935-70-3; **8b**, 73935-69-0; **9**, 10321-86-5; 11, 88946-44-5; **12**, 73935-73-6; N-phenylbenzhydrazidoyl chloride, 15224-14-3; N-benzyl-p-nitrobenzimidoyl chloride, 3712-57-0; 1,2,3,5-tetramethylbenzene, 527-53-7.

Gas-Phase Basicities of Substituted Styrenes. Comparison of Gas-Phase and Solution Reactivities

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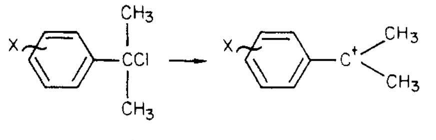
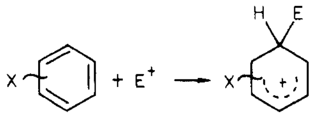
Received May 13, 1983

One of the most successful quantitative treatments for the understanding of organic reactions in solution has been the use of the Brown–Hammett σ^+ constants for the correlation of electrophilic reactivity.[2] These parameters are defined[3] in terms of the solvolysis of cumyl chlorides at 25 °C (eq 1) by the equation log $k(X)/k(H) = -4.54\sigma^+$.

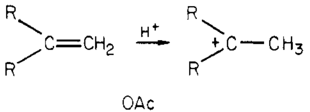


(1)

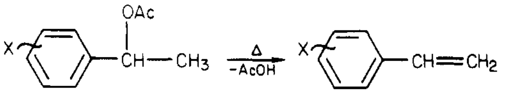
The σ^+ constants derived from eq 1 account quite successfully for a variety of electrophilic aromatic substitution reactions, as illustrated in eq 2. These constants also have been found to correlate reactivities in a variety of other systems, including the rates of protonation of aliphatic alkenes (eq 3),[4] and the gas-phase pyrolysis of 1-arylethyl acetates to form styrenes (eq 4).[5]



(2)



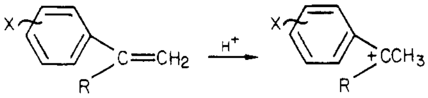
(3)



(4)

With the increasing availability of values of gas-phase heats of reaction[6] as well as the heats of formation of carbocations in solution,[7] it has become increasingly possible to evaluate the contributions of ion stability and solvation to organic reactivity and to compare the rates of reaction in solution with heats of reaction. A notable achievement in this field was the measurement of the gas-phase basicities of substituted benzenes.[8a] These were found to be correlated very well with the σ^+ constants, which was a powerful indication that these empirically derived quantities did, in fact, provide a quantative measure of substituent effects on cation stability. The thermodynamics of these reactions also can be accounted for by molecular orbital calculations.[8b,9]

The correlations of the rates of protonation of styrenes in solution (eq 5) is another case where the σ^+ constants have been very successful.[10] The relations between the sensitivity of the reaction to the substituents X, which is measured by the ρ^+ values, and the electron-donating ability of the substituent R, as measured by the σ^+ value of this group, also has been revealing. It has been found[10h] that when R is strongly electron-donating (HO,[10d] MeO[10e], EtO[10f]), ρ^+ has values between −1 and −2, whereas when R is strongly electron-withdrawing (CF_3), ρ^+ is −4.0.[10h] Intermediate situations exist when R = H (ρ^+ = −2.9,[10b] −3.6[10c,i]), and R = Me (ρ^+ = −2.9[10a,b]).



(5)

1, R = H
2, R = CH_3

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