

To this day it is not known with certainty why the perylene-iodine complexes, or in this case the BBT (1)-iodine complexes, conduct electricity. Since both perylene-bromine and -iodine complexes are good conductors, one can probably rule out conductivity by the halogen because there are no known polybromides which are conductors. Also, all well-known organic conductors exhibit a high degree of transport along segregated, partially charged stacks of donors and/or acceptors.⁹ On the other hand, iodine clathrates (presumably containing iodine chains)¹⁰ exhibit some conductivity (ρ on the order of 10^4 - 10^5 Ω cm),¹¹ but these resistivity values are much higher than the low resistivity exhibited by the above complexes. It is possible that the conductivity in the above complexes is due to a combination of effects: iodine chains and stacked, partially charged donors. The final proof has to rest with an X-ray structure determination. This is quite imperative, since there is no reliable X-ray structure available for Per_xI_y .¹²⁻¹⁴ Large single crystals of (BBT) I_3 suitable for a solid-state structure determination were grown from chloroform solution¹⁶ and their solid-state structure is currently under investigation.

In conclusion, and contrary to expectations, BBT is virtually identical with perylene with the exception of a hypsochromic shift in its electronic absorption and emission spectra and a higher reactivity toward electrophilic substitution.

Experimental Section

Preparation of 3,4:3',4'-Bibenzothiophene (1). A solution of anthraquinone 1,5-dithiolate was prepared by the procedure developed by Jenny¹⁵ for the preparation of the 1,4 isomer. To this solution was added an excess of chloroacetic acid. The mixture was heated to reflux for ca. 2 h, filtered, cooled, acidified with hydrochloric acid, and centrifuged (the precipitated, crude diacid was found to be virtually impossible to filter). The muddy, green residue was washed with water, ethanol, and ether and

allowed to dry. Since it was virtually insoluble in all common organic solvents, it was not purified further but was used directly in the next step.

A suspension of 5.7 g of the above diacid in 228 mL of anhydride was heated to reflux (bath temperature ca. 168 °C). A fine stream of gas evolved. After 1.5 h of refluxing, the mixture was filtered hot. As the filtrate cooled, yellowish crystals separated. The crude crystals were chromatographed on 40 mL of Al_2O_3 (Woelm grade I) with carbon disulfide as eluent. The first band contained pure 1 as yellow platelets: 1.67 g; 43% yield; mp 294.6-295.9 °C subl; mass spectrum m/e 264 (P), 132 (base peak); NMR (CS_2) δ 7.0-7.5, m.

Iodine Complex. Attempts to grow an iodine complex from chloroform solution by slow diffusion in an inverted U-tube failed. Slow cooling of a chlorobenzene solution afforded small, black lustrous needles. The supernatant solution was decanted and the solid was washed four times with a small amount of hexane to remove residual chlorobenzene. The hexane washings were always slightly purple, indicating that some iodine was being washed away with the residual chlorobenzene. The solid was then dried under a fast stream of nitrogen and analyzed. As expected,³ BBT forms more than one phase in its reaction with iodine. So far, the compounds (BBT) $\text{I}_{2.4}$ and (BBT) I_3 ¹⁶ have been isolated. Several elemental analyses of the (BBT) $\text{I}_{2.4}$ phase gave average values: C, 33.67; H, 1.15; I, 53.50; S, 11.19. These correspond to (BBT) $\text{I}_{2.4\pm 0.2}$ (calcd for $\text{C}_{16}\text{H}_8\text{I}_{2.4}\text{S}_2$: C, 33.75; H, 1.40; I, 53.58; S, 11.25). While the analysis agreement for this nonstoichiometric formulation is excellent, we know it cannot correspond to the highly conducting complex because we found that room-temperature conductivity decreased with increasing hexane washings (decreasing I_2 content).¹⁷ More careful in-house analyses of (BBT) $\text{I}_{2.4}$ gave the same results, indicating that conventional microanalytical techniques are not sensitive enough to detect the minor changes in stoichiometry which give rise to noticeable changes in conductivity.

A small sample of (BBT) $\text{I}_{2.4}$ was placed in a vacuum oven (~100 torr) at ca. 40 °C for ca. 48 h. When the yellowish brown residue was suspended in methylene chloride, the solvent became slightly purple-brown and the solid became bright yellow. The melting point of this yellow, crystalline residue indicated it was unchanged BBT.

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Registry No. 1, 70160-67-7; 6, 70160-68-8; 6 S,S-diacetic acid, 70160-69-9; naphthalene, 91-20-3; benzo[b]thiophene, 95-15-8; benzo[c]thiophene, 270-82-6; perylene, 198-55-0; chloroacetic acid, 79-11-8; 1 iodine complex, 70160-70-2.

(9) H. J. Keller, Ed., "Chemistry and Physics of One Dimensional Metals", NATO Advanced Study Institutes Series, Plenum Press, New York, 1977.

(10) However, see R. C. Teitelbaum, S. L. Ruby, and T. J. Marks, *J. Am. Chem. Soc.*, **100**, 3215 (1978), for reinterpretation in terms of I_5^- .

(11) M. M. Labes, *Org. Solid State, Proc. Int. Symp.*, **5th**, (1978).

(12) The X-ray structure analysis on perylene-iodine complexes as performed by Uchida¹³ is quite confusing and most probably wrong since there is evidence from Raman spectroscopy that there are I_5^- units in perylene-iodine.¹⁴

(13) T. Uchida and H. Akamatu, *Bull. Chem. Soc. Jpn.*, **34**, 1015 (1961).

(14) T. J. Marks, private communication, July 1978.

(15) W. Jenny, *Helv. Chim. Acta*, **41**, 317 (1958).

(16) M. M. Labes and H. I. Kao, private communication.

(17) The same behavior was observed with perylene iodine.³

Thione S-Imides. Reaction with the Carbon-Carbon Double Bond: 1,3-Dipolar and Diels-Alder-Type Cycloaddition and Ene Reactions

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Thione S-imide (1) reacted as a 1,3 dipole with enamine (5), vinyl ethers (2), bicyclo olefins (10, 12), and cyclopentadiene (18) to give 1,3 dipolar cycloadducts, while with acyclic dienes (14) the imide reacted as a dienophile to give Diels-Alder-type cycloadducts. Furthermore, the imide and (1-cyclohexenyl)amines (7) afforded ene-reaction products.

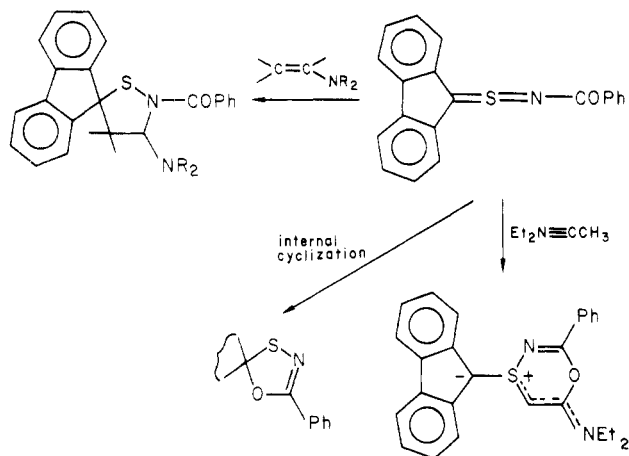
In our previous work, thione S-imides (1) were readily prepared by a Wittig-type reaction of phosphonium ylides

with *N*-sulfinyl-*p*-toluenesulfonamide, and some cycloaddition reactions of 1 were described briefly.^{1,2} Recently,

Table I. 1,2-Thiazolidines (3)

compd	yield, %	mp, °C	NMR, δ (NCHO)
3a	94	172.5-173.5	5.95
3b	84	152.0-153.0	5.88
3c	95	167.5-168.5	5.92
3d	87	180.0-180.5	6.01

this new kind of heterocumulene has also been prepared by other workers³⁻⁸ but there are only a few examples of cycloaddition reactions of the imides. Burgess et al.⁵ reported that the reaction of *N*-benzoyl-*S*-(9-fluorenylidene)sulfilimine with enamines and a ynamine gave isothiazolidines and oxathiazine, respectively. However, the reactions with electrophiles such as phenyldiazomethane and diphenylketene and with less reactive nucleophiles such as vinyl ethers and ketene acetals were unsuccessful. In these cases, only internal cyclization of the imide took place.



In the present study, we have examined the reaction of moderately stable thione *S*-imides **1** with various dipolarophiles containing carbon-carbon double bond(s) and have found that the imides (**1**) underwent a variety of reactions such as 1,3 dipolar, ene, and Diels-Alder-type reactions.

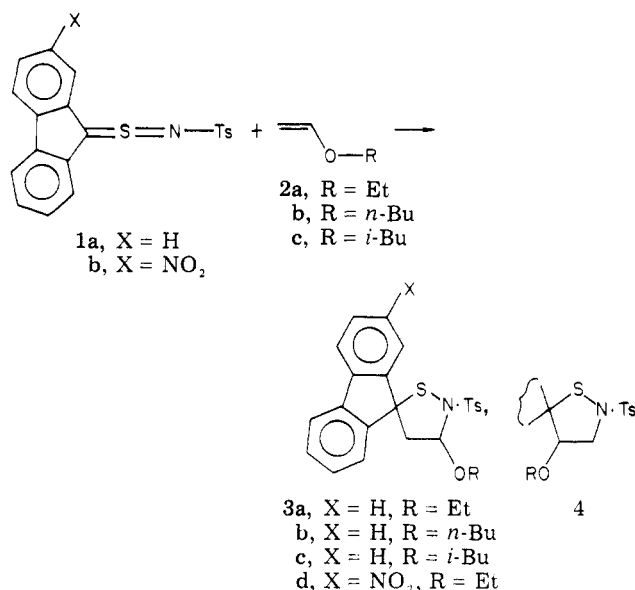
Results and Discussion

Reaction of Thione *S*-Imides **1** with Vinyl Ethers

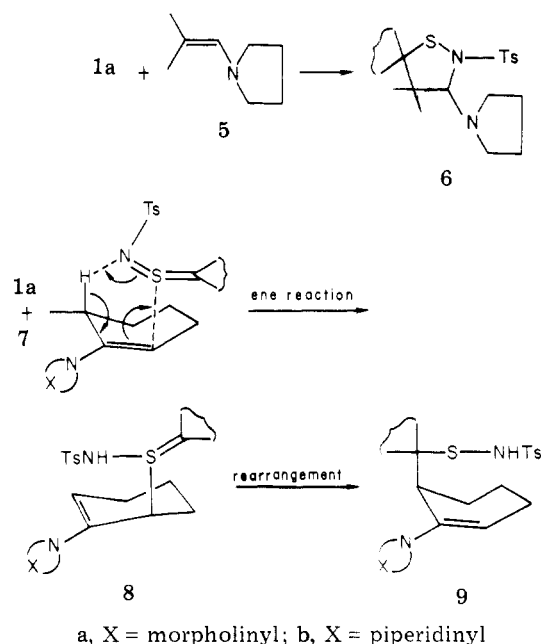
2. As described in the previous paper,² **1** reacted with **2** to give 1,3-dipolar cycloadducts in fairly good yields (Scheme I; Table I). The structure of the adducts was assigned as **3**, and not the alternative regioisomer **4**, on the basis of their NMR spectra. The methine proton at the 3 position appeared at considerably low field (δ 5.88-6.01) because of the marked deshielding effect of electronegative nitrogen and oxygen atoms. Although stereoisomers are possible in the case of **3d**, the configuration of **3d** obtained could not be confirmed.

Reaction of Thione *S*-Imide **1a with Enamines **5** and **7**.** Similar to Burgess' imide,⁵ **1a** reacted with enamine **5** to give 1:1 cycloadduct **6**. Although a clear NMR spectrum of **6** could not be obtained due to the instability of the adduct in solution, elemental analysis and the IR

Scheme I



Scheme II



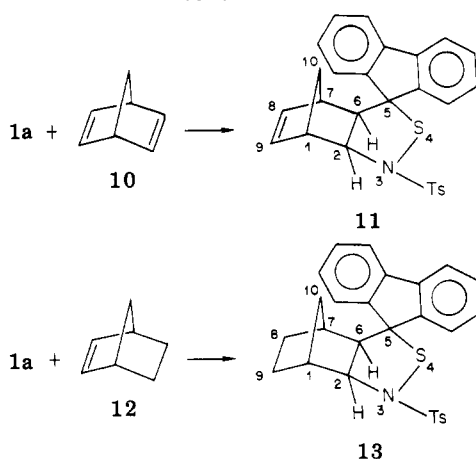
spectrum supported the 1,2-thiazolidine structure **6**. On the other hand, the reaction of **1a** with enamine **7** gave the unexpected 1:1 acyclic adduct **8** or **9**. The assignment of these structures is based on the following: the ν (N-H) absorption band at 3320 cm⁻¹; ν (C=C) (alkene) at 1665-1660 cm⁻¹; the absence of ν (S=N) in the region of 900-1000 cm⁻¹; the presence of an olefinic proton at δ 5.38 as triplet signals. Although structure **9** is more probable than ylidic **8**, it has been difficult to distinguish them. The formation of these adducts presumably involves ene reaction of **1a** with **7** followed by rearrangement (Scheme II).^{9,10}

(1) T. Saito and S. Motoki, *J. Org. Chem.*, **42**, 3922 (1977).
 (2) T. Saito and S. Motoki, *Chem. Lett.*, 591 (1978).
 (3) S. Tamagaki and S. Oae, *Tetrahedron Lett.*, 1159 (1972).
 (4) S. Tamagaki, K. Sakaki, and S. Oae, *Bull. Chem. Soc. Jpn.*, **47**, 3084 (1974).
 (5) E. M. Burgess and H. R. Penton, Jr., *J. Org. Chem.*, **39**, 2885 (1974); *J. Am. Chem. Soc.*, **95**, 279 (1973).
 (6) S. Holm, J. A. Boerma, N. H. Nilsson, and A. Senning, *Chem. Ber.*, **109**, 1069 (1976).
 (7) I. Crossland, *Acta Chem. Scand., Ser. B*, **31**, 890 (1977).
 (8) A. Tangerman and B. Zwanenburg, *Tetrahedron Lett.*, 259 (1977).

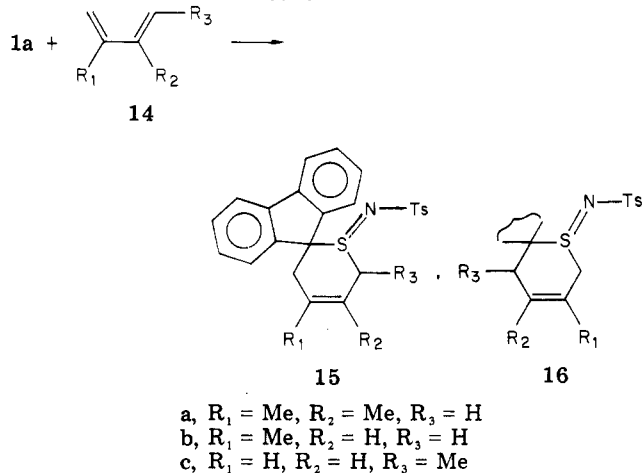
(9) Similar reactions of some heterocumulenes with the C=C bond have been reported in the literature: (a) E. G. Kataev, V. V. Plemenkov, *Zh. Org. Khim.*, **2**, 1124 (1966); *Chem. Abstr.*, **65**, 15429d; (b) K. B. Sharpless and T. Hori, *J. Org. Chem.*, **41**, 176 (1976); (c) T. Hori, S. P. Singer, and K. B. Sharpless, *ibid.*, **43**, 1456 (1978); (d) N. N. Schönberger and G. Kresze, *Justus Liebigs Ann. Chem.*, 1725 (1975); (e) M. M. Rogic and D. Masilamani, *J. Am. Chem. Soc.*, **99**, 5219 (1977).

(10) In contrast with this ene-reaction product, zwitterionic product from the reaction of sulfine (fluorene-thione *S*-oxide) with **7a** has been reported. W. A. Sheppard and J. Diekmann, *J. Am. Chem. Soc.*, **86**, 1891 (1964).

Scheme III



Scheme IV



Reaction of Thione S-Imide 1a with Norbornadiene (10) and Norbornene (12). Reactive bicyclo olefins such as **10** and **12** underwent 1,3-dipolar cycloaddition reaction with **1a**. In the case of **10** an exo monoadduct **11** was obtained together with a small amount of fluorenone formed by the decomposition of **1a** (Scheme III).

It is reasonable for the exo structure that the coupling constants between the bridgehead proton (H(1) or H(7)) and the adjacent angular proton (H(2) or H(6)) of **11** are very small (1.2 Hz).¹¹ The mass spectrum of **11** showed evidence for the retro Diels-Alder reaction to cyclopentadiene and 1,2-thiazoline (an intense ion at m/e 391 for $M^+ - \text{cyclopentadiene}$).

Similar treatment of **1a** with **12** also afforded an exo adduct **13**. Such exo addition is well-known in 1,3-dipolar cycloadditions.^{12,13} Attempts to perform the reaction of **1a** with normal olefins such as 1-pentene, styrene, cy-

(11) (a) H. Günter and G. Jikeii, *Chem. Rev.*, **77**, 599 (1977), and references cited therein; (b) E. I. Snyder and B. Franzus, *J. Am. Chem. Soc.*, **86**, 1166 (1964); (c) P. Laszlo and P. v. P. Schleyer, *ibid.*, **86**, 1171 (1964).

(12) (a) R. Huisgen, R. Grashey, and J. Sauer, "The Chemistry of Alkenes", S. Patai, Ed., Interscience, London, 1964, p 806; (b) G. Bianchi, C. D. Micheli, and R. Gandolfi, "Supplement A: The Chemistry of Double-Bonded Functional Groups", S. Patai, Ed., *ibid.*, 1977, p 369, and references cited therein; (c) H. R. Barton and M. J. Robson, *J. Chem. Soc., Perkin Trans. 1*, 1245 (1974).

(13) Some 1,3 dipoles react with **10** to give a small amount of endo adducts in contrast with the case of **12**; however, no conspicuous difference between **10** and **12** was observed in the present results. (a) H. Taniguchi, T. Ikeda, Y. Yoshida, and E. Imoto, *Bull. Chem. Soc. Jpn.*, **50**, 2694 (1977); (b) *ibid.*, **51**, 1495 (1978); (c) S. McLean and D. M. Findlay, *Tetrahedron Lett.*, 2219 (1969); (d) D. M. Findlay, M. L. Roy, and S. McLean, *Can. J. Chem.*, **50**, 3186 (1972).

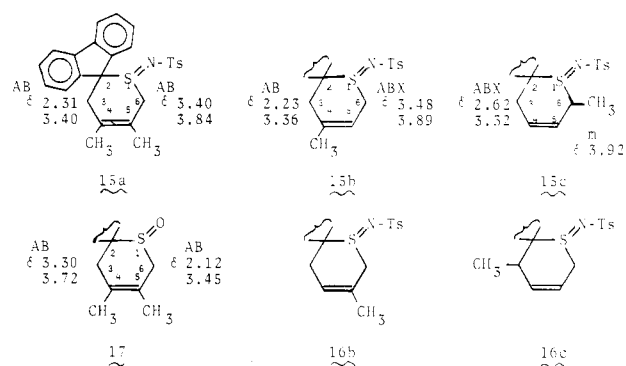


Figure 1.

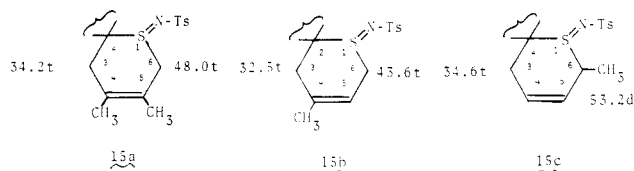


Figure 2.

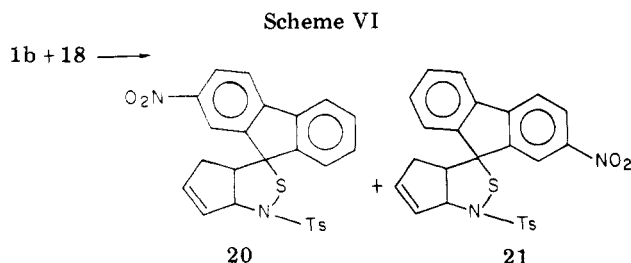
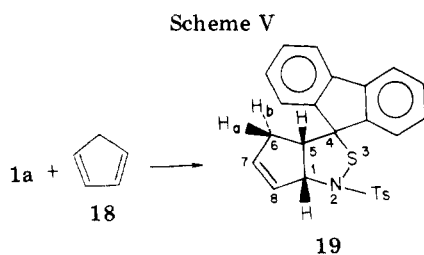
clohexene, and cyclooctadiene and with electron-poor olefins such as acrylonitrile, ethyl acrylate, and maleic anhydride were all unsuccessful.

Reaction of Thione S-Imide 1a with Dienes 14. In our preliminary communication,² we reported Diels-Alder-type reactions of **1a** with acyclic dienes **14b,c** and considered the structure of the adducts to be **16b,c** (Scheme IV). In the NMR spectrum of **16b**, ABX-type methylene signals at δ 3.48 and 3.89 were assigned to the protons at C(3) and AB type ones at δ 2.23 and 3.36 to the C(6) protons, respectively. These assignments were based on comparison with the NMR spectral data of the related compound **17** in which the methylene protons at C(6) (adjacent to S=O) appeared upfield from those at C(3).¹⁴ The adduct from **14c** was similarly considered to be **16c**. However, it is more reasonable that the absorption of the methylene protons adjacent to the electron-withdrawing S=O or S=NTs group appears downfield from those adjacent to the fluorenylidene group. If this assumption is correct, the assignment of the protons of both the methylenes becomes reversed and the adducts from **14b** and **14c** are not **16b,c** but **15b,c**.

This conclusion is also consistent with the ¹³C NMR spectral measurement of the adducts. Both **15a** and **15b** showed two sets of signals due to the methylene carbons as triplets in the single frequency off-resonance decoupling (SFORD) spectra. The assignment of the methylene carbons at C(6) (adjacent to the sulfur atom) to the lower field resonance (**15a**, δ 48.0; **15b**, δ 43.6) is consistent with the substituent shift induced by the electron-withdrawing S=NTs group and therefore the other methylene carbons at C(3) are assigned to the higher field resonance (**15a**, δ 34.2; **15b**, δ 32.5). So the chemical shift (δ 34.6 t) was rationally assigned to the methylene carbon at C(3) in **15c** because the carbon chemical shifts of the methylene carbons of **15c** would remain unchanged from those of **15a** and **15b**.

Reaction of Thione S-Imides 1 with Cyclopentadiene (18). In contrast with acyclic dienes **14**, cyclopentadiene reacted with **1a** rapidly to afford the unexpected 1,3-dipolar cycloadduct **19**. The adduct showed $\nu(\text{C}=\text{C})$ absorption but no characteristic strong

(14) B. Zwanenburg, L. Thijs, J. B. Boens, and J. Strating, *Recl. Trav. Chim. Pays-Bas*, **91**, 443 (1972).



$\nu(\text{S}=\text{N})$ absorption band in the IR spectrum. The ^{13}C NMR spectrum showed an allylic carbon signal (C(6)) at δ 35.5 but absence of a signal of bridging methylene carbon at δ 48–50.¹⁵

The ^1H NMR spectrum of the adduct exhibited two methine signals at δ 3.56 (H(1)) and 5.52 (H(5)) along with two nonequivalent methylene (δ 2.26, 2.08) and two olefinic proton (δ 5.84, 5.97) signals. The absorption of H(1) appeared downfield from that of H(5) on account of deshielding by the adjacent electron-withdrawing N-Ts group. Assignment of the couplings ($J_{1,5} = 7.4$, $J_{5,6a} = 7.4$, $J_{5,6b} = 3.0$ Hz in H(5) and $J_{1,5} = 7.4$, $J_{1,8} = 1.8$, $J_{1,6a} = 1.8$ Hz (long range) in H(1)) can be reasonably resolved for the structure 19 (Scheme V). Similar treatment of 1b with 18 gave the adducts 20 and 21 (Scheme VI). The configuration of the stereoisomers could not be confirmed.

Generally, heterocumulenes having a central quadrivalent sulfur atom, $\text{X}=\text{S}=\text{Y}$, behave as 1,3 dipoles or dienophiles in cycloaddition reactions with olefins and dienes, and relationships between such alternative reactivity of the cumulene $\text{X}=\text{S}=\text{Y}$ and the electronegativities of the ligands (X, Y) have been proposed by Inagaki et al.^{16,17} According to their proposal, thione S-imide is a 1,3 dipole. However, we have found that the thione S-imide 1 indeed reacted as both a 1,3 dipole and a dienophile. This suggests that reactivity of 1 would lie on the borderline of those of a 1,3 dipole and a dienophile due to the electronic effect of the substituents attached to the nitrogen (*p*-toluenesulfonyl) and carbon atoms (fluorenylidene).

Experimental Section

All melting points are uncorrected. IR spectra were measured on a Hitachi Model 260-10 spectrophotometer. ^1H NMR and ^{13}C NMR spectra were measured on a JEOL JNM-FX 100 spec-

(15) (a) E. Breitmaier, G. Haas, and W. Voelten, "Atlas of Carbon-13 NMR Data", Vol 1,IFI/Plenum, Heyden & Son Ltd., 1976; (b) D. C. Dittmer, J. E. McCaskie, J. E. Babiarz, and M. V. Ruggeri, *J. Org. Chem.*, **42**, 1910 (1977); (c) J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972.

(16) Y. Inagaki and R. Okazaki, *Yuki Gosei Kagaku Kyokai Shi*, **36**, 1 (1978).

(17) In fact, thiocarbonyl ylides, *N*-thiosulfinylamines, and Burgess' thione S-imide react as 1,3 dipoles, and sulfines, *N*-sulfinylamines, and sulfur diimides are dienophiles. (a) J. Butter, S. Wassenaar, and R. M. Kellogg, *J. Org. Chem.*, **37**, 4045 (1972); (b) R. M. Kellogg, *Tetrahedron*, **32**, 2165 (1976); (c) ref 12c; (d) Y. Inagaki, R. Okazaki, and N. Inamoto, The 36th National Meeting of the Chemical Society of Japan, 2S 38, 1977; (e) ref 5; (f) ref 14; (g) G. Kresze, A. Maschke, R. Albrecht, K. Bederke, H. P. Patzschke, H. Smalla, and A. Trede, *Angew. Chem., Int. Ed. Engl.*, **1**, 89 (1962); (h) G. Kresze and W. Wucherpfennig, *ibid.*, **6**, 149 (1967); *Tetrahedron Lett.*, 1671 (1966); E. S. Levtschenko and Ya. G. Bol'no, *Zh. Org. Khim.*, **1**, 150, 305 (1965).

trometer in δ values from Me_4Si as an internal standard in deuteriochloroform. Mass spectra were recorded on a Hitachi double-focusing RMU-7M mass spectrometer operating at an ionizing potential of 70 eV.

Elemental analyses were performed with a Shimadzu UM-3B universal organic microanalyzer and a Shimadzu NA-1 rapid-nitrogen analyzer.

Reaction of Thione S-Imides 1 with Vinyl Ethers 2. To a partially suspended solution of 1.83 g (5 mmol) of 1a in anhydrous 1,2-dichloroethane (50 mL) an equimolar amount of 2 in dry 1,2-dichloroethane (10 mL) was added dropwise with stirring at room temperature (20–25 °C). The red suspension of 1a gradually disappeared within 2–3 h, after which the reaction mixture was allowed to stand overnight to complete the reaction. After evaporation of the solvent, the residue was washed with ether and recrystallized from benzene (3a–c) or benzene-dichloromethane (3d) to give 3a–c as colorless crystals and 3d as yellowish crystals in good yields. Additional 3a–d was obtained from the mother liquor. When amounts of decomposed products of 1, such as 9,9'-bis(fluorenylidene), fluorenone, and *p*-toluenesulfonamide, were found in the reaction mixture by a TLC check, column chromatography on silica gel (Wako gel C-200) with benzene (3d, followed by dichloromethane) as eluent was employed to give analytically pure 3a–d.

3a: yield 94%; mp 172.5–173.5 °C dec; IR (KBr disk) 1290, 1170, 1095 ($\nu(\text{SO}_2)$), 1110 ($\nu(\text{C}-\text{O})$), 990 cm^{-1} ; NMR (CDCl_3) δ 8.2–6.6 (m, 12 H, aromatic), 5.95 (q, 1 H, $J = 5.0$ Hz, NCHO), 4.01 (dq, ABX₃ type (half), $J = 10.0$, $J = 6.9$ Hz, OCH_2CH_3), 3.62 (dq, ABX₃ type (half), $J = 10.0$, $J = 6.9$ Hz, OCH_2CH_3), 2.50 (s, 3 H, CH_3 (Ts)), 2.62 (q, 1 H, $J = 17.5$, $J = 5.0$ Hz, CH_2), 2.43 (q, 1 H, $J = 17.5$, $J = 1.5$ Hz, CH_2), 1.38 (t, 3 H, $J = 6.9$ Hz, OCH_2CH_3); mass spectrum m/e (relative intensity) 437 (17, M^+), 392 (4, $\text{M}^+ - \text{Ts}$), 359 (7, $\text{M}^+ - \text{OEt} - \text{HS}$), 204 (100, $\text{M}^+ - \text{Ts} - \text{OEt} - \text{HS}$).

Anal. Calcd for $\text{C}_{24}\text{H}_{23}\text{NO}_3\text{S}_2$: N, 3.20; S, 14.63. Found: N, 3.19; S, 14.45.

3b: yield 84%; mp 152.0–153.0 °C dec; IR (KBr disk) 1305, 1170, 1095 ($\nu(\text{SO}_2)$), 1110 ($\nu(\text{C}-\text{O})$), 970 cm^{-1} ; NMR (CDCl_3) δ 8.2–6.5 (m, 12 H, aromatic), 5.88 (q, 1 H, $J = 4.7$, $J = 1.0$ Hz, NCHO), 3.92 (dt, 1 H, $J = 10.0$, $J = 6.2$ Hz, OCH_2), 3.52 (dt, 1 H, $J = 10.0$, $J = 6.2$ Hz, OCH_2), 2.56 (q, $J = 14.0$, $J = 4.7$ Hz, CH_2), 2.36 (q, $J = 14.0$, $J = 1.0$ Hz, CH_2), 2.43 (s, CH_3 (Ts)), 2.0–1.1 (m, 4 H, CH_2CH_2), 0.96 (t, 3 H, $J = 6.5$, $\text{CH}_2\text{CH}_2\text{CH}_3$); mass spectrum m/e 465 (9, M^+), 392 (3, $\text{M}^+ - \text{OBu}-n$), 359 (4, $\text{M}^+ - \text{OBu}-n - \text{HS}$), 310 (13, $\text{M}^+ - \text{Ts}$), 204 (100, $\text{M}^+ - \text{OBu}-n - \text{Ts} - \text{HS}$).

Anal. Calcd for $\text{C}_{26}\text{H}_{27}\text{NO}_3\text{S}_2$: C, 67.07; H, 5.85; N, 3.01; S, 13.77. Found: C, 66.77; H, 5.85; N, 2.95; S, 13.66.

3c: yield 95%; mp 167.5–168.5 °C dec; IR (KBr disk) 1300, 1170, 1095 ($\nu(\text{SO}_2)$), 1110 ($\nu(\text{C}-\text{O})$), 970 cm^{-1} ; NMR δ 8.3–6.6 (m, 12 H, aromatic), 5.92 (q, 1 H, $J = 4.5$, $J = 1.5$ Hz, NCHO), 3.73 (q, 1 H, $J = 9.5$, $J = 6.5$ Hz, OCH_2CH), 3.34 (q, 1 H, $J = 9.5$, $J = 6.5$ Hz, OCH_2CH), 2.65 (q, $J = 13.0$, $J = 4.5$ Hz, CH_2), 2.34 (q, 1 H, $J = 13.0$, $J = 1.5$ Hz, CH_2), 2.51 (s, CH_3 (Ts)), 2.03 (sept, 1 H, $J = 6.6$ Hz, $\text{CH}_2\text{CH}(\text{CH}_3)_2$), 1.02 (d, 3 H, $J = 6.6$ Hz, CH_3), 1.00 (d, 3 H, $J = 6.6$ Hz, CH_3); mass spectrum m/e 465 (11, M^+), 392 (3, $\text{M}^+ - \text{OBu}-i$), 359 (5, $\text{M}^+ - \text{OBu}-i - \text{HS}$), 310 (8, $\text{M}^+ - \text{Ts}$), 204 (100, $\text{M}^+ - \text{OBu}-i - \text{Ts} - \text{HS}$).

Anal. Calcd for $\text{C}_{26}\text{H}_{27}\text{NO}_3\text{S}_2$: C, 67.07; H, 5.85; N, 3.01; S, 13.77. Found: C, 67.10; H, 5.87; N, 3.01; S, 13.77.

3d: yield 87%; mp 180.0–180.5 °C dec; IR (KBr disk) 1520, 1340 ($\nu(\text{NO}_2)$), 1295, 1165, 1095 ($\nu(\text{SO}_2)$), 1110 ($\nu(\text{C}-\text{O})$), 970 cm^{-1} ; NMR δ 8.3–7.0 (m, 10 H, aromatic), 9.08 (d, 1 H, $J = 2$ Hz, aromatic), 6.01 (dd, $J = 5.0$, $J = 1.5$ Hz, 1 H, NCHO), 4.05 (dq, 1 H, $J = 7.0$, $J = 10.0$, OCH_2CH_3), 3.65 (dq, 1 H, $J = 7.0$, $J = 10.0$ Hz, OCH_2CH_3), 2.74 (q, $J = 17.5$, $J = 5.0$ Hz, CH_2), 2.48 (q, $J = 17.5$, $J = 1.5$, CH_2), 2.54 (s, 3 H, CH_3 (Ts)), 1.49 (t, 3 H, $J = 7.0$, CH_3); mass spectrum m/e 482 (47, M^+), 437 ($\text{M}^+ - \text{OEt}$), 404 (3, $\text{M}^+ - \text{OEt} - \text{HS}$), 327 (52, $\text{M}^+ - \text{Ts}$), 249 (21, $\text{M}^+ - \text{OEt} - \text{Ts} - \text{HS}$), 91 (100, $\text{OEt} - \text{HS}$).

Anal. Calcd for $\text{C}_{24}\text{H}_{22}\text{N}_2\text{O}_5\text{S}_2$: C, 59.75; H, 4.60; N, 5.81; S, 13.29. Found: C, 59.80; H, 4.64; N, 5.71; S, 13.20.

Reaction of Thione S-Imide 1a with 1-(Pyrrolidinyl)-2-methyl-1-propene (5). To 1.83 g (5 mmol) of 1a in 30 mL of 1,2-dichloroethane-ether (1:2 vol %) an equimolar amount of 5 in 10 mL of 1,2-dichloroethane was slowly added dropwise with

stirring at -18°C . The red color of the solution gradually disappeared and turned to blue. The reaction mixture was carefully concentrated in vacuo and the residue was triturated with ether at low temperature. Care should be taken to exclude moisture. Recrystallization from dichloromethane-ether at low temperature gave **6** as colorless crystals in 50% yield; mp $111.0\text{--}113.0^{\circ}\text{C}$ dec; IR (KBr disk) 1600, 1450, 1345, 1160, 1090 ($\nu(\text{SO}_2)$) cm^{-1} .

Anal. Calcd for $\text{C}_{28}\text{H}_{30}\text{N}_2\text{O}_2\text{S}_2$: N, 5.71. Found: N, 5.62.

Reaction of Thione S-Imide 1a with N-(1-cyclohexenyl)amines 7. To 1.83 g (5 mmol) of **1a** in 30 mL of 1,2-dichloroethane an equimolar amount of **7** in 10 mL of 1,2-dichloroethane was slowly added dropwise with stirring at temperatures between -16 and -18°C . After the mixture was stirred for an additional period, evaporation of the solvent in vacuo and crystallization of the residue from dichloromethane-ether at low temperature gave **9a,b** (or **8a,b**) as colorless crystals in 78 and 47% yields, respectively.

A small amount of *p*-toluenesulfonamide was obtained from the mother liquor.

9a (8a): yield 78%; mp $111.5\text{--}112.5^{\circ}\text{C}$ dec; IR (KBr disk) 3320 ($\nu(\text{N-H})$), 1660 ($\nu(\text{C}=\text{C})$), 1285, 1165, 1095 ($\nu(\text{SO}_2)$) cm^{-1} ; NMR δ 7.9–7.1 (m, 12 H, aromatic), 7.0 (s, 1 H, NH), 5.38 (t, 1 H, $J = 4$ Hz, olefinic proton), 3.75 (t, 4 H, $J = 5$ Hz, OCH_2), 3.35, 3.08 (dt, 4 H, $J = 16$, $J = 5$ Hz, NCH_2), 2.37 (s, 3 H, CH_3 (Ts)), 2–1 (m, 6 H, $(\text{CH}_2)_3$); mass spectrum m/e 445 (22, $\text{M}^+ - \text{morpholine}$), 290 (60, $\text{M}^+ - \text{morpholine} - \text{Ts}$), 196 (34, $\text{Fl}=\text{S}^+$).

Anal. Calcd for $\text{C}_{30}\text{H}_{32}\text{N}_2\text{O}_3\text{S}_2$: N, 5.26. Found: N, 5.21.

9b (8b): yield 47%; mp $104.2\text{--}104.5^{\circ}\text{C}$ dec; IR (KBr disk) 3320 ($\nu(\text{N-H})$), 1660 ($\nu(\text{C}=\text{C})$), 1160, 1090 ($\nu(\text{SO}_2)$) cm^{-1} ; NMR (CDCl_3) δ 8.1–7.0 (m, 12 H, aromatic), 2.37 (s, CH_3 (Ts)), 3–0.8 (m, methylenes); mass spectrum m/e 360 (2, $\text{M}^+ - \text{TsNH}_2$).

Anal. Calcd for $\text{C}_{31}\text{H}_{34}\text{N}_2\text{O}_2\text{S}_2$: N, 5.28. Found: N, 5.20.

Reaction of Thione S-Imide 1a with Norbornadiene (10). A mixture of 0.92 g (2.5 mmol) of **1a** and a large excess **10** in 20 mL of dry 1,2-dichloroethane was stirred at room temperature for about a day. After the color of **1a** disappeared, the solvent was concentrated in vacuo and the residue was triturated with ether to afford **11** in 52% yield. Recrystallization from dichloromethane gave analytically pure **11** as colorless needles: mp $222\text{--}224^{\circ}\text{C}$; IR (KBr disk) 1630 vw ($\nu(\text{C}=\text{C})$), 1445, 1350, 1160, 1095 ($\nu(\text{SO}_2)$), 1075, 965 cm^{-1} ; NMR δ 7.9–6.5 (m, 11 H, aromatic), 6.00 (dt, 1 H, $J = 8.0$, $J = 1.0$ Hz, aromatic), 6.22 (d, 1 H, $J = 3.5$ Hz, olefinic proton), 6.13 (d, 1 H, $J = 3.5$ Hz, olefinic proton), 4.58 (dt, 1 H, $J = 7.0$, $J = 1.2$, $J = 1.2$ Hz, endo H(2)), 3.47 (s of m, 1 H, bridgehead H(1)), 3.19 (d of m, 1 H, $J = 9.1$ Hz, $J =$ very small, bridging anti H(10)), 2.98 (s of m, 1 H, bridgehead H(7)), 2.67 (dd, 1 H, $J = 7.0$, $J = 1.8$ Hz, endo H(6)), 2.52 (s, 3 H, CH_3 (Ts)), 1.85 (dt, 1 H, $J = 9.1$, $J = 1.8$, $J = 1.8$ Hz, bridging syn H(10)); mass spectrum m/e 457 (10, M^+), 425 (1, $\text{M}^+ - \text{S}$), 391 (27, $\text{M}^+ - \text{cyclopentadiene}$), 302 (6, $\text{M}^+ - \text{Ts}$), 236 (100, $\text{M}^+ - \text{Ts} - \text{cyclopentadiene}$), 196 (5, $\text{Fl}=\text{S}^+$).

Anal. Calcd for $\text{C}_{27}\text{H}_{23}\text{NO}_2\text{S}_2$: C, 70.88; H, 5.07; N, 3.06; S, 14.01. Found: C, 70.60; H, 5.10; N, 2.92; S, 13.97.

Reaction of Thione S-Imide 1a with Norbornene (12). A mixture of 0.92 g (2.5 mmol) of **1a** and a large excess of **12** was allowed to stir for a day at room temperature. After evaporation of the solvent in vacuo, the residue was subjected to column chromatography on silica gel (Wako gel C-200), using benzene (followed by dichloromethane) as eluent to afford **13** as colorless crystals (recrystallized from dichloromethane-ether) in 68% yield: mp $222\text{--}224^{\circ}\text{C}$; IR (KBr disk) 1600, 1300, 1160, 1095 ($\nu(\text{SO}_2)$), 980 cm^{-1} ; NMR δ 7.9–7.1 (m, 10 H, aromatic), 6.70 (dt, 1 H, $J = 8.0$, $J = 1.0$ Hz, aromatic), 6.06 (dt, 1 H, $J = 8.0$ Hz, $J =$ small, aromatic), 4.36 (d, 1 H, $J = 8.0$ Hz, endo H(2)), 2.97 (br s, 1 H, bridgehead H(1)), 2.76 (d of m, 1 H, $J = 11$ Hz, $J =$ small, bridging H(10) anti to ethylene bridge), 2.52 (s, 3 H, CH_3 (Ts)), ca. 2.5 (obscured, 1 H, bridgehead H(7)), 2.45 (d, 1 H, $J = 8.0$ Hz, endo H(6)), 1.7–0.8 (m, 5 H, CH_2CH_2 , syn H(10)); mass spectrum m/e 459 (30, M^+), 304 (90, $\text{M}^+ - \text{Ts}$), 238 (100, $\text{M}^+ - \text{Ts} - \text{cyclopentene}$), 203 (21, $\text{M}^+ - \text{Ts} - \text{cyclopentene} - \text{S}$).

Anal. Calcd for $\text{C}_{27}\text{H}_{25}\text{NO}_2\text{S}_2$: C, 70.57; H, 5.48; N, 3.05; S, 13.93. Found: C, 70.60; H, 5.49; N, 3.03; S, 13.91.

Reaction of Thione S-Imide 1a with Dienes 14. A mixture of **1a** (0.92 g, 2.5 mmol) and a large excess of **14** in 50 mL of 1,2-dichloroethane was stirred at room temperature. The red suspended **1a** dissolved within 2 h, and the mixture was allowed

to stand overnight to complete the reaction (**b**, for 2 days; **c**, for 6 days). After evaporation of the solvent in vacuo, the residue was column chromatographed on silica gel, using benzene as eluent to give small amounts of colored decomposed products of **1a**, 9,9'-bis(fluorenylidene), and fluorenone. The second elution with chloroform (or dichloromethane) afforded **15a-c** as colorless crystals in (**a**) 61% (recrystallized from benzene), (**b**) 94% (benzene), and (**c**) 62% (dichloromethane-ether) yields, respectively.

15a: mp $147.0\text{--}147.5^{\circ}\text{C}$; IR (KBr disk) 1670 ($\nu(\text{C}=\text{C})$), 1275, 1140, 1090 ($\nu(\text{SO}_2)$), 960 ($\nu(\text{S}=\text{N})$) cm^{-1} ; ^1H NMR δ 7.8–6.8 (m, 12 H, aromatic), 3.40, 3.84 AB type (dd, 2 H, $J = 17$ Hz, SCH_2), 3.40, 2.31 (dd, 2 H, $J = 17$ Hz, CH_2), 2.29 (s, 3 H, CH_3 (Ts)), 1.89 (s, 3 H, CH_3), 1.81 (s, 3 H, CH_3); ^{13}C NMR δ 62.2 s (C(2)), 34.2 t (C(3)), 48.0 t (C(6)), 19.5 q, 20.5 q ($\text{CH}_3(\text{C}(4,5))$), 21.3 q (CH_3 (Ts)); mass spectrum m/e 447 (1, M^+), 292 (2, $\text{M}^+ - \text{Ts}$), 276 (44, $\text{M}^+ - \text{TsNH}_2$), 261 (100, $\text{M}^+ - \text{TsNH}_2 - \text{CH}_3$), 91 (82, ToI^+).

Anal. Calcd for $\text{C}_{26}\text{H}_{25}\text{NO}_2\text{S}_2$: C, 69.78; H, 5.63; N, 3.13; S, 14.30. Found: C, 69.83; H, 5.63; N, 3.13; S, 14.27.

15b: mp $132.0\text{--}132.4^{\circ}\text{C}$; IR (KBr disk) 1680 ($\nu(\text{C}=\text{C})$), 1285, 1145, 1095 ($\nu(\text{SO}_2)$), 980 ($\nu(\text{S}=\text{N})$) cm^{-1} ; ^1H NMR δ 7.75–6.90 (m, 12 H, aromatic), 5.64 (s of m, 1 H, olefinic proton), 3.89, 3.48 ABX type (dd of m, $J = 19$ Hz, $J =$ small, SCH_2), 3.36, 2.23 AB type (dd, $J = 17$ Hz, CH_2), 2.28 (s, CH_3 (Ts)), 1.86 (s, 3 H, CH_3); ^{13}C NMR δ 62.3 s (C(2)), 32.5 t (C(3)), 43.6 t (C(6)), 24.8 q ($\text{CH}_3(\text{C}(4))$), 21.2 q (CH_3 (Ts)); mass spectrum m/e 433 (1, M^+), 278 (3, $\text{M}^+ - \text{Ts}$), 262 (53, $\text{M}^+ - \text{TsNH}_2$), 247 (100, $\text{M}^+ - \text{TsNH}_2 - \text{CH}_3$), 91 (69, ToI^+).

Anal. Calcd for $\text{C}_{25}\text{H}_{23}\text{NO}_2\text{S}_2$: C, 69.27; H, 5.35; N, 3.23; S, 14.78. Found: C, 69.18; H, 5.39; N, 3.16; S, 14.61.

15c: mp $144.2\text{--}144.4^{\circ}\text{C}$; IR (KBr disk) 1670 ($\nu(\text{C}=\text{C})$), 1285, 1150, 1095 ($\nu(\text{SO}_2)$), 980 ($\nu(\text{S}=\text{N})$) cm^{-1} ; ^1H NMR δ 7.6–6.7 (m, 12 H, aromatic), 6.08 (dq, 1 H, $J = 10.8$, $J = 4.8$, $J = 2.4$ Hz, $=\text{CHCH}_2$), 5.82 (q, 1 H, $J = 10.8$, $J = 1.5$ Hz, $=\text{CHCH}_2$), 3.92 (m, 1 H, CHCH_2), 3.32 ABX type (half) (d of m, 1 H, $J = 20$ Hz, CH_2), 2.62 ABX type (half) (q, 1 H, $J = 20$, $J = 4.8$ Hz, CH_2), 2.32 (s, 3 H, CH_3 (Ts)), 1.58 (d, 3 H, $J = 7.8$ Hz, CH_3); ^{13}C NMR δ 66.8 s (C(2)), 34.6 t (C(3)), 53.2 d (C(6)), 16.0 q ($\text{CH}_3(\text{C}(6))$), 21.3 q (CH_3 (Ts)); mass spectrum m/e 433 (3, M^+), 278 (7, $\text{M}^+ - \text{Ts}$), 262 (18, $\text{M}^+ - \text{TsNH}_2$), 247 (14, $\text{M}^+ - \text{TsNH}_2 - \text{CH}_3$), 91 (100, ToI^+).

Anal. Calcd for $\text{C}_{25}\text{H}_{23}\text{NO}_2\text{S}_2$: C, 69.27; H, 5.35; N, 3.23; S, 14.78. Found: C, 69.41; H, 5.47; N, 3.24; S, 14.80.

Reaction of Thione S-Imide 1a with Cyclopentadiene (18). To 0.92 g (2.5 mmol) of **1a** in 1,2-dichloroethane **18** was added dropwise for 10 min with stirring at room temperature. After additional stirring of the mixture and evaporation of the solvent, the residue was washed with ether and recrystallized from dichloromethane-ether to give **19** as colorless crystals in 83% yield: mp $206.5\text{--}207.5^{\circ}\text{C}$; IR (KBr disk) 1660 vw ($\nu(\text{C}=\text{C})$), 1350, 1165, 1095 ($\nu(\text{SO}_2)$) cm^{-1} ; ^1H NMR δ 7.95–7.10 (m, 12 H, aromatic), 5.97, 5.84 (dd of m, 2 H, $J = 6.0$, $J = 1.8$, $J = 1.8$ Hz, olefinic protons), 5.52 (dt, 1 H, $J = 7.4$, $J = 1.8$, $J = 1.8$ Hz, bridgehead H(1)), 3.56 (dt, 1 H, $J = 7.4$, $J = 7.4$, $J = 3.0$ Hz, bridgehead H(5)), 2.48 (s, 3 H, CH_3 (Ts)), 2.26 (d of m, 1 H, $J = 20.5$, $J = 7.4$ Hz, CH_2), 2.08 (d of m, 1 H, $J = 20.5$, $J = 3.0$ Hz, CH_2) [spin-decoupling measurements were performed at the center of H(1), H(5), and H(6), respectively, for the assignment]; ^{13}C NMR δ 77.5 d (C(1)), 71.1 s (C(4)), 56.7 d (C(5)), 35.5 t (C(6)), 21.6 q (CH_3); mass spectrum m/e 431 (18, M^+), 276 (100, $\text{M}^+ - \text{Ts}$), 210 (19, $\text{M}^+ - \text{Ts} - \text{cyclopentadiene}$), 91 (14, ToI^+).

Anal. Calcd for $\text{C}_{25}\text{H}_{21}\text{NO}_2\text{S}_2$: C, 69.59; H, 4.91; N, 3.25; S, 14.86. Found: C, 69.44; H, 4.90; N, 3.07; S, 14.80.

Reaction of Thione S-Imide 1b with Cyclopentadiene (18). A mixture of 0.35 g (0.835 mmol) of **1b** and a large excess of **18** in 1,2-dichloroethane 40 mL was stirred overnight at room temperature. After the usual workup recrystallization from dichloromethane-ether gave **20** and **21** in 91% yield. This mixture of stereoisomers was then subjected to column chromatography on silica gel (Wako gel C-200), using benzene as eluent to give **20** (former elution) and **21** (later elution) in the ratio ca. 4:3. **20:** mp $215\text{--}216^{\circ}\text{C}$; IR (KBr disk) 1520, 1340 ($\nu(\text{NO}_2)$), 1160, 1090 ($\nu(\text{SO}_2)$); ^1H NMR δ 8.55–7.30 (m, 11 H, aromatic), 6.00 (d of m, $J = 6.0$ Hz, 1 H, olefinic H(8)), 5.89 (d of m, $J = 6.0$ Hz, 1 H, olefinic H(7)), 5.65 (dt, 1 H, $J = 7.5$, $J = 1.8$, $J = 1.8$ Hz, bridgehead H(1)), 3.69 (dt, 1 H, $J = 7.5$, $J = 7.5$, $J = 1.8$ Hz,

bridgehead H(5)), 2.36 (dd of m (half), 1 H, $J = 18$, $J = 7.5$, $J = 1.8$ Hz, H(6)), 2.50 (s, 3 H, CH₃ (Ts)), 1.84 (d of m, 1 H, $J = 18$ Hz, H(6)); ¹³C NMR δ 77.7 d (C(1)), 71.3 s (C(4)), 57.0 d (C(5)), 35.5 t (C(6)), 21.7 q (CH₃); mass spectrum m/e 476 (24, M⁺), 321 (100, M⁺ - Ts), 288 (5, M⁺ - Ts - HS), 255 (9, M⁺ - Ts - cyclopentadiene).

Anal. Calcd for C₂₅H₂₀N₂O₄S₂: C, 63.02; H, 4.23; N, 5.88; S, 13.44. Found: C, 62.91; H, 4.26; N, 5.81; S, 13.29.

21: mp 207–208 °C; IR (KBr disk) 1520, 1340 (ν (NO₂)), 1160, 1090 (ν (SO₂)); ¹H NMR δ 8.8–7.3 (m, 11 H, aromatic), 5.90 (s of m, 2 H, olefinic H(7,8)), 5.59 (d of m, 1 H, $J = 7.5$, $J = 2.4$, $J = 1.2$ Hz, bridgehead H(1)), 3.69 (dt, 1 H, $J = 7.5$, $J = 7.5$, $J = 2.0$ Hz, bridgehead H(5)), 2.49 (s, 3 H, CH₃ (Ts)), 2.36 (dd of m (half), 1 H, $J = 18$, $J = 7.5$, H(6)), 1.98 (d of m, 1 H, $J = 18$ Hz, H(6));

¹³C NMR δ 77.9 d (C(1)), 71.2 s (C(4)), 56.1 d (C(5)), 35.6 t (C(6)), 21.6 q (CH₃); mass spectrum m/e 476 (24, M⁺), 321 (100, M⁺ - Ts), 288 (5, M⁺ - Ts - HS), 255 (9, M⁺ - Ts - cyclopentadiene).

Anal. Calcd for C₂₅H₂₀N₂O₄S₂: C, 63.02; H, 4.23; N, 5.88; S, 13.44. Found: C, 63.05; H, 4.25; N, 5.90; S, 13.32.

Registry No. 1a, 63609-88-1; 1b, 63609-89-2; 2a, 109-92-2; 2b, 111-34-2; 2c, 109-53-5; 3a, 68380-36-9; 3b, 68380-37-0; 3c, 68380-38-1; 3d, 70179-31-6; 5, 2403-57-8; 6, 70179-32-7; 7a, 670-80-4; 7b, 2981-10-4; 8a, 70179-33-8; 8b, 70179-34-9; 9a, 70179-35-0; 9b, 70179-36-1; 10, 121-46-0; 11, 70208-93-4; 12, 498-66-8; 13, 70179-37-2; 14a, 513-81-5; 14b, 78-79-5; 14c, 504-60-9; 15a, 70179-38-3; 15b, 70179-39-4; 15c, 70179-40-7; 16b, 68380-34-7; 16c, 68380-35-8; 18, 542-92-7; 19, 70179-41-8; 20, 70179-42-9; 21, 70223-54-0.

Novel Rearrangement of a [2.2](2,5)Pyrrolophane

William W. Paudler,* Robert L. Mahaffey, and J. L. Atwood

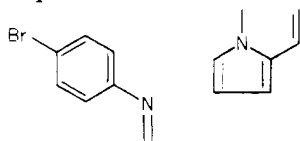
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Received January 17, 1979

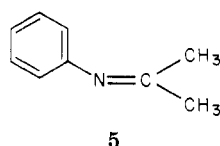
N-(*p*-Bromophenyl)[2.2](2,5)pyrrolophane (1), when treated with acid, forms, successively, 13-(*p*-bromophenyl)-13,14-diazatetracyclo[8.2.1.1^{4,7}.0^{1,14}]tetradeca-4,6,11-triene and its 2,6,11-triene isomer (4). A possible mechanism, involving an aziridinium ion intermediate, is suggested.

We have recently described¹ the synthesis of *N*-(*p*-bromophenyl)[2.2](2,5)pyrrolophane (1) from *N*-(*p*-bromophenyl)-3,6-dioxo-[8](2,5)pyrrolophane (2) and ammonium acetate (Scheme I). Compound 1 was formed, along with an isomeric material, identified as 13-(*p*-bromophenyl)-13,14-diazatetracyclo[8.2.1.1^{4,7}.0^{1,14}]tetradeca-4,6,11-triene (3), and could also be obtained from compound 2 by treatment with ammonium acetate in dilute aqueous acid.

In some instances, this reaction afforded traces of an additional isomer (4) which is isomeric with compounds 1 and 3. We have now found that a solution of compound 3 in acetic acid, when heated, or in trifluoroacetic acid at room temperature affords this "trace" material in essentially quantitative yield. The ¹H NMR spectrum of this compound is very similar to that of compound 3 except for minor chemical shift changes (cf. Table I). On the other hand, its ultraviolet spectrum [λ_{\max} 253, 292, 301 (sh) nm] is significantly different from that of compound 3 (λ_{\max} 262 nm). The surprising appearance of these new long-wavelength absorptions in compound 4 can reasonably be explained by the presence of a highly conjugated chromophore. Since compound 3 has two aromatic rings within its structure (phenyl and pyrrole), one might suggest that a double-bond migration into conjugation with either one of these rings has occurred. This would give rise to either one of the partial structures



Since the ultraviolet spectrum of the Schiff base 5³ is



5

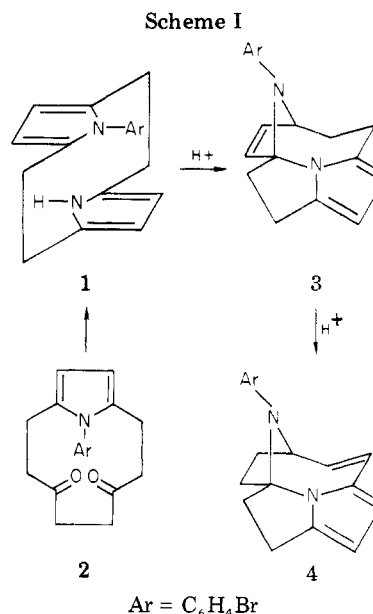


Table I. Crystal Data

compd	C ₁₈ N ₂ H ₁₇ Br
mol wt	341.3
μ	28.61 cm ⁻¹
ρ (obsd)	1.50 (2) g cm ⁻³
ρ (calcd)	1.49 g cm ⁻³
max crystal dimensions	0.30 × 0.45 × 0.50 mm
space group	<i>P</i> 2 ₁
<i>Z</i>	2
cell constants	
<i>a</i>	6.991 (5) Å
<i>b</i>	10.497 (6) Å
<i>c</i>	10.452 (6) Å
β	98.10 (4) ^o
<i>V</i>	759.43 Å ³

significantly different from that of compound 4, the conjugated pyrrole partial structure is a much more at-

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