

11, 77507-18-7; 12, 77507-19-8; 13, 77507-20-1; 14, 77507-21-2; 15, 77507-22-3; 16, 77507-23-4; 17, 77507-24-5; 18, 77507-25-6; (\pm)-19, 77507-26-7; 20, 77507-27-8; 21, 77507-28-9; 22, 77507-29-0; 23, 77507-30-3; 24, 77507-31-4; 25, 77507-32-5; 26, 77520-25-3; 27, 77507-33-6; 28, 77507-34-7; 29, 77507-35-8; 30, 77507-36-9; 31,

77507-37-0; 32, 77507-38-1; 33, 77507-39-2; (\pm)-35a, 77507-40-5; (\pm)-35b, 77507-41-6; (\pm)-35c, 77507-42-7; (\pm)-35d, 77507-43-8; 36, 77507-44-9; 37, 77507-45-0; 38, 77507-46-1; 39, 77507-47-2; (\pm)-40, 77507-48-3; (\pm)-41, 77507-49-4; (\pm)-42, 77507-50-7; (\pm)-43, 77507-51-8.

Some Novel Transformations of 1,4-Dithiafulvenes

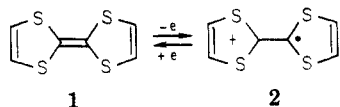
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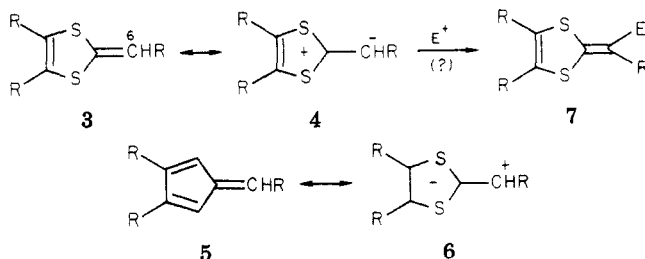
Received March 12, 1981

6-Phenyl-1,4-dithiafulvenes have been substituted at the 6-position by bromo, phenylazo, and nitroso groups; cation radical intermediates are proposed in these reactions. The 6-nitroso derivatives are deoxygenated by phosphines to give products derived from the fragmentation of intermediary nitrenes.

The chemistry of tetrathiafulvalene (1, TTF) and its derivatives has been the object of intense interest during the past decade, as a result of the ability of TTF to undergo a reversible one-electron oxidation to give a stable cation-radical (2), many salts of which show unusual electrical conductivity in the solid state.¹



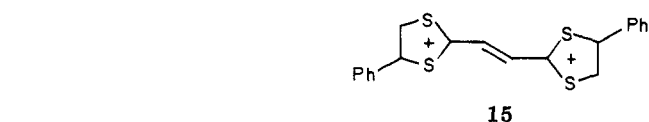
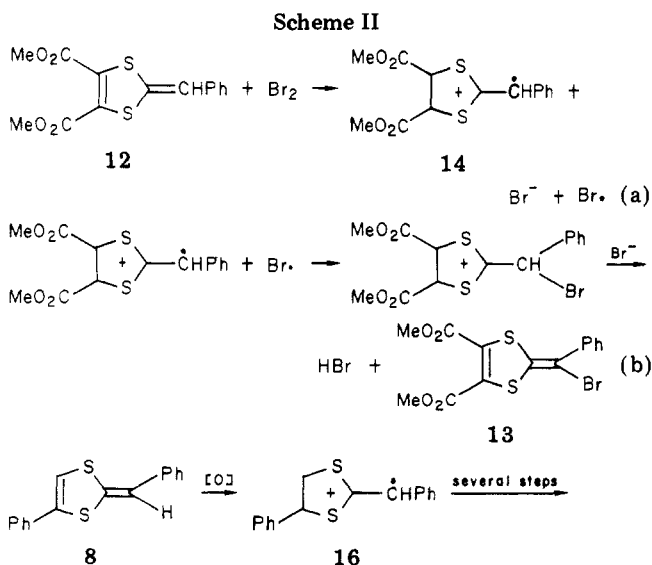
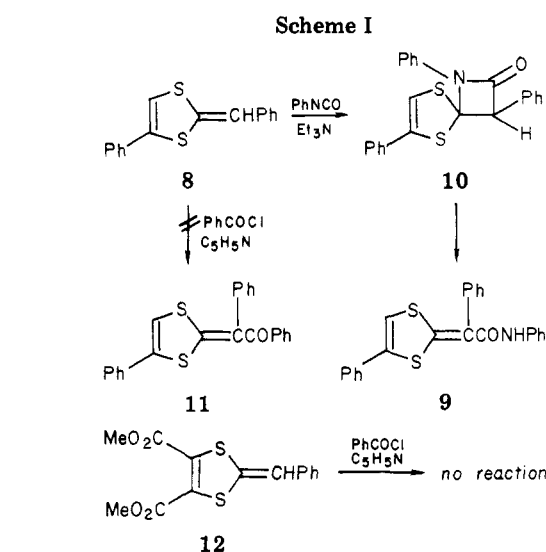
The rather closely related 1,4-dithiafulvene system 3 should be stabilized by the 1,3-dithiolium ylide contributor 4, in contrast to carbocyclic fulvenes 5 in which the cy-



clopentadienide form 6 is the important charge-separated contributor. It might be predicted, therefore, that 1,4-dithiafulvenes would undergo attack by electrophiles at the exocyclic carbon to give 6-substituted derivatives of the type 7. In this paper, we report the results of a study initiated by a search for such substitution reactions.²

Results and Discussion

Substitution Reactions of 1,4-Dithiafulvenes. The first 1,4-dithiafulvenes which were reported in 1958 were obtained by the photolysis of 1,2,3-thiadiazoles.³ One of these compounds, the trans isomer of 2,6-diphenyl-1,4-dithiafulvene (8) was later found to react slowly with hot phenyl isocyanate in the presence of triethylamine to give the 6-carboxamide derivative 9⁴ (Scheme I). The con-



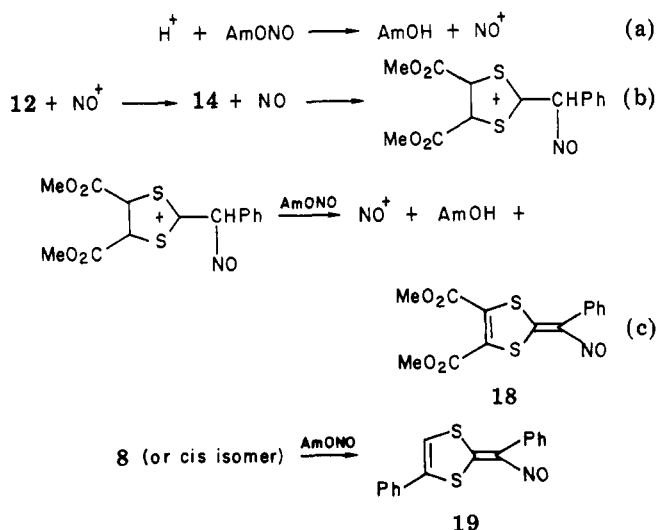
(1) For general reviews on this subject see: (a) A. F. Garito and A. G. Heeger, *Acc. Chem. Res.*, **7**, 232 (1974); (b) E. M. Engler, *CHEM TECH*, **6**, 274 (1976); (c) M. Narita and C. U. Pittman, Jr., *Synthesis*, 489 (1976).

(2) A preliminary account of this work was presented in a Plenary Lecture delivered at the 7th International Heterocyclic Conference held in Tampa, FL, Aug 1979 [M. P. Cava and M. V. Lakshmikantham, *J. Heterocycl. Chem.*, **17**, S-39 (1980)].

(3) W. Kirmse and L. Horner, *Justus Liebigs Ann. Chem.*, **614**, 4 (1958).

version of 8 to 9, which represents the only reported substitution reaction of a 1,4-dithiafulvene, at first appears

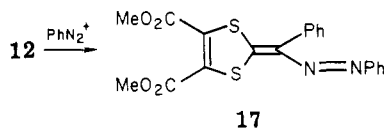
Scheme III



to involve nucleophilic attack of fulvene **8** on phenyl isocyanate, but it more likely proceeds by a cycloaddition of the fulvene to the isocyanate, followed by a base-promoted cleavage of the intermediary β -lactam **10**. In indirect support of this view, we have found that the benzoylation of **8** by benzoyl chloride and pyridine does not yield ketone **11**, the starting fulvene being recovered unchanged. Similarly, the readily available 2,3-bis(carbomethoxy)-6-phenyl-1,4-dithiafulvene (**12**) is recovered unchanged after heating with benzoyl chloride and pyridine.

In contrast to this result, fulvene **12** was found to react readily with bromine in carbon tetrachloride solution to give the corresponding 6-bromo derivative **13**. The unexpected ease of bromination of **12** has led us to postulate that this bromination proceeds by way of an electron-transfer mechanism involving the cation radical **14**, as shown in Scheme II. Such a mechanism is in accord with the known facile oxidation of the diphenyl-dithiafulvene **8** to the dimeric dication **15**, a reaction assumed to proceed by way of the unstable intermediary cation-radical **16**.^{3,5}

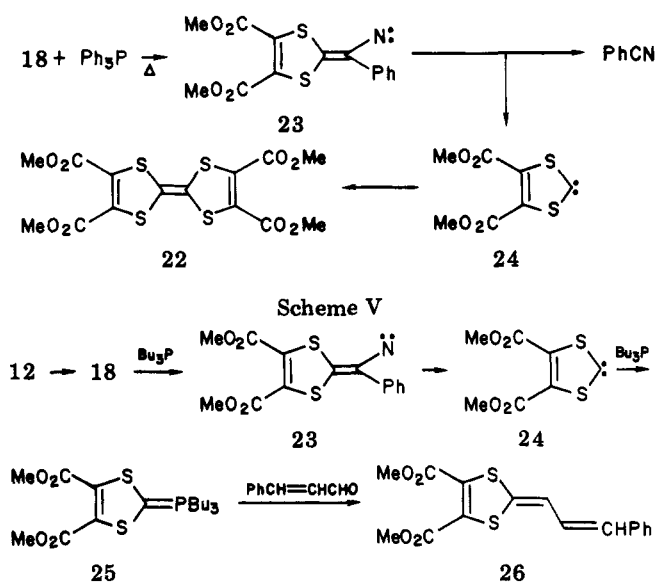
A second substitution reaction of fulvene **12** was found in its rapid coupling with benzenediazonium fluoroborate in dimethylformamide solution to give the red-orange azo compound **17**. Again, the reaction may be rationalized



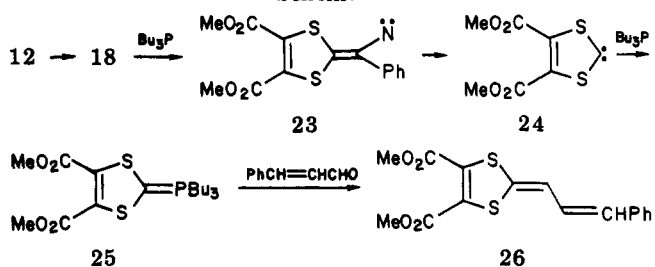
as an electron-transfer process, the initial step being the oxidation of fulvene **12** to the cation radical **14**, which then couples with the resulting benzenediazonium radical.⁶

The most remarkable reaction of fulvene **12** was its rapid conversion to the bright green nitroso derivative **18** by the action of excess amyl nitrite in cold dichloromethane solution. The diphenylfulvene **8** undergoes an analogous transformation to give dark green crystals of a nitroso derivative, probably the trans isomer **19**. The reaction of **12** with amyl nitrite was found to be accelerated by traces

Scheme IV

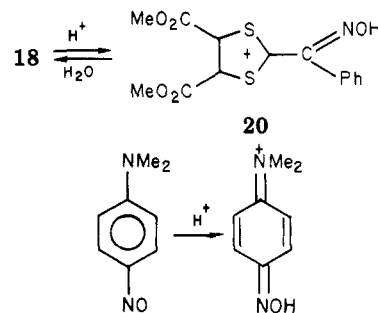


Scheme V



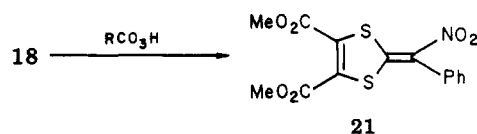
of acid and inhibited by tertiary amines, thus implying the generation of the nitrosonium ion as the initial step of the nitrosation. We believe that the weakly electrophilic nitrosonium ion is not bringing about a direct substitution of **12** but that an electron-transfer mechanism is again operative as shown in Scheme III. It may be noted that the nitric oxide intermediate is known to be an extremely effective radical trap.⁷

Transformations of 6-Nitroso-1,4-dithiafulvenes. Protonation of the nitroso diester **18** by strong mineral acid results in the formation of a yellow cation, which is hydrolyzed by water with the regeneration of the green nitroso compound **18**. The protonation of **18** parallels the



well-known O-protonation of *p*-nitrosodimethylaniline to give a yellow cation; the cation derived from **18** is therefore assigned the oxime structure **20**.

Oxidation of **18** takes place more rapidly at the nitroso function than at the heterocyclic sulfurs. Thus, the green ester **18** reacts rapidly with *m*-chloroperbenzoic acid to give the corresponding bright yellow nitro compound **21**.



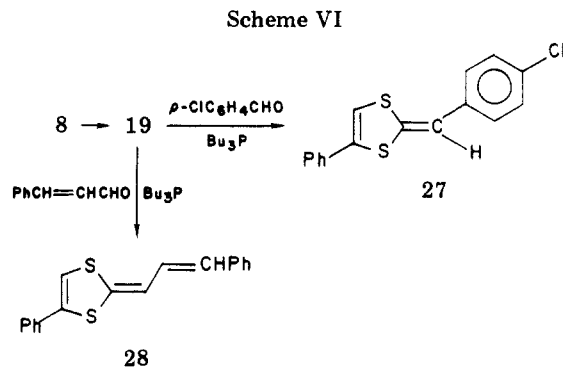
Diester **18** was destroyed when it was heated in refluxing acetonitrile with triphenylphosphine. The two products isolated from this reaction were benzonitrile and tetrakis(carbomethoxy)tetrathiafulvalene (**22**). These products

(4) H. Spies, K. Gewald, and R. Mayer, *J. Prakt. Chem.* **313**, 804 (1971).

(5) R. Mayer and H. Kröber, *J. Prakt. Chem.* **316**, 907 (1974).

(6) Evidence for a similar mechanism in the classical coupling of diazonium ions with phenoxides has been reported recently: N. N. Bubnov, K. A. Bilevitch, L. Poljakova, and O. Y. Okhlobystin, *J. Chem. Soc., Chem. Commun.*, 1058 (1972).

(7) For the use of NO as a radical trap, see J. E. Leffler, "The Reactive Intermediates of Organic Chemistry", Interscience, New York, 1956, p 66-68.



apparently result by a phosphine deoxygenation of the nitroso function of 18 to give the nitrene 23,⁸ which fragments to benzonitrile and the carbene 24; dimerization of 24 then affords 22 (Scheme IV).

The same fragmentation reaction of 18 takes place under milder conditions with the more reactive tributylphosphine as the oxygen abstractor. If an excess of the phosphine is employed in the presence of cinnamaldehyde, the carbene 24 is trapped by the phosphine to generate the unstable phosphorane 25 (Scheme V), which reacts in situ with the cinnamaldehyde to give the new fulvene 26 in 21% yield.⁹ The overall conversion of the benzylidene fulvene 12, via its nitroso derivative 18, to the cinnamylidene analogue 26 constitutes a novel "transfulvenation" synthesis.

Since 26 is easily prepared by a more direct method,⁹ its synthesis from 12 is primarily of mechanistic interest. However, the transfulvenation synthesis seems to be of more general applicability, and it can be used to prepare dithiafulvenes which cannot be readily obtained in other ways. For example, diphenylnitrosofulvene 19 and *p*-chlorobenzaldehyde yield the monochloro analogue 27 of the precursor fulvene 8 (Scheme VI), while 19 and cinnamaldehyde afford 28, which is a vinylogue of 8. Fulvene 8 is a very accessible starting material, since it may be prepared in a simple two-step sequence by starting from acetophenone semicarbazone.^{10,11}

Experimental Section

General Methods. Melting points are determined on a Thomas-Hoover melting point apparatus and are uncorrected. Mass (70 EV) and UV-visible spectra (MeCN) were obtained on Perkin-Elmer 270B and 202 instruments, respectively. Analyses were performed by Galbraith Laboratories.

Reaction of Dithiafulvene 8 with Benzoyl Chloride. A solution of *cis*-dithiafulvene 8¹¹ (0.26 g) in methylene chloride (5 mL) was treated with benzoyl chloride (0.4 g). The mixture was left at room temperature for 12 h; the solvent was evaporated to dryness in vacuo, and the residue was triturated with methanol to yield *trans*-dithiafulvene 8 [0.20 g, 76.9% yield; mp 206 °C (lit.³ mp 206 °C)] identical with an authentic sample (melting point, mixture melting point, and IR spectrum).

Reaction of Dithiafulvene 12 with Benzoyl Chloride/Pyridine. The foregoing reaction was carried out in a similar manner on dithiafulvene 12⁹ (0.6 g). Workup led to the recovery of fulvene 12 (0.42 g, 70%).

Action of Bromine on Fulvene 12. A solution of fulvene 12 (0.60 g) in methylene chloride (5 mL) was treated with a solution of bromine (0.3 g) in carbon tetrachloride (3 mL) at room temperature. After the evolution of hydrogen bromide ceased, the

solvent was removed in vacuo. Crystallization of the residue from methylene chloride-hexane afforded orange needles (0.60 g, 79%) of bromofulvene 13: mp 92 °C; mass spectrum, *m/e* (relative intensity) 388 (*M*⁺, 100), 386 (90); UV-vis λ_{max} 235 nm (log ϵ 4.25), 275 (3.96), 319 (3.77), 350 (3.9). Anal. Calcd for C₁₄H₁₁BrO₄S₂: C, 43.42; H, 2.94; S, 16.57. Found: C, 43.19; H, 2.94; S, 16.57.

Reaction of Fulvene 12 with Benzenediazonium Fluoroborate. A solution of diester fulvene 12 (0.44 g) in dimethylformamide (5 mL) was treated with excess benzenediazonium fluoroborate (0.40 g). The mixture warmed up slowly and turned dark red. After 10 min, it was diluted with water, and the red precipitate was filtered, washed, and dried. Crystallization from methanol containing chloroform afforded salmon pink crystals of the fulvene azo dye 17: 0.40 g (68%); mass spectrum, *m/e* (relative intensity) 412 (*M*⁺, 10); UV-vis λ_{max} 245 nm (log ϵ 4.29), 288 (4.11), 450 (4.21); λ_{max} (MeCN-HBF₄) 230 (log ϵ 4.67), 255 (4.42), 520 (4.58). Anal. Calcd for C₂₀H₁₆N₂O₄S₂: C, 58.23; H, 3.91; N, 6.79. Found: C, 58.16; H, 4.28; N, 6.76.

Nitrosofulvene 18. To a solution of diester fulvene 12 (15.0 g) in methylene chloride (150 mL) cooled in ice was added in portions with swirling excess isoamyl nitrite (23 mL). The mixture was set aside at room temperature for 0.75 h and then was concentrated under reduced pressure. Addition of methanol to the dark green concentrate induced crystallization. After the mixture was chilled, the bright green crystals of nitrosofulvene 18 were filtered, washed with more methanol and anhydrous ether, and dried (11.65 g, 71% yield). This sample was pure and had a melting point of 165 °C dec. An analytical sample prepared by recrystallization from methanol containing methylene chloride exhibited the same melting point: mass spectrum, *m/e* (relative intensity) 337 (*M*⁺, 15); UV-vis λ_{max} 225 nm (log ϵ 4.15), 270 (4.00), 430 (4.00); λ_{max} (MeCN-HBF₄) 229 (log ϵ 4.64), 330 (br, 3.82), 375 (3.75). Anal. Calcd for C₁₄H₁₁NO₅S₂: C, 49.86; H, 3.29; N, 4.15. Found: C, 49.79; H, 3.30; N, 4.01.

Nitrosofulvene 19. A solution of *cis*-fulvene 8¹¹ (2.68 g) in methylene chloride (25 mL) was treated at room temperature with isoamyl nitrite (2.5 mL). After 1 h the green crystals were filtered and crystallized from nitromethane to yield shiny emerald green needles of nitrosofulvene 19: 1.80 g (62%); mp > 195 °C dec; mass spectrum, *m/e* (relative intensity) 293 (*M*⁺, 5); UV-vis λ_{max} 243 nm (log ϵ 4.50), 440 (4.31); λ_{max} (MeCN-HBF₄) 227 (4.82), 280 (infl, 4.18), 386 (4.10). Anal. Calcd for C₁₆H₁₁NOS₂: C, 64.65; H, 3.73; N, 4.71. Found: C, 64.64; H, 3.72; N, 4.65.

Diester Nitrofulvene 21. Diester nitrosofulvene 18 (0.70 g) in methylene chloride (15 mL) containing aqueous disodium hydrogen phosphate (1.4 g in 30 mL of H₂O) was treated with a solution of *m*-chloroperbenzoic acid (0.5 g of 76% pure acid) in methylene chloride (5 mL) at room temperature with stirring. Within 0.75 h all the peracid was consumed. The resulting yellow organic layer was separated and washed successively with aqueous sodium bicarbonate and water. Evaporation followed by crystallization of the residue from methanol furnished diester nitrofulvene 21: 0.65 g (88%); mp 134–136 °C. An analytical sample was prepared by recrystallization once from hexane-methylene chloride to give yellow crystals: mp 135–136 °C; mass spectrum, *m/e* (relative intensity) 353 (*M*⁺, 100); UV-vis λ_{max} 225 nm (log ϵ 4.8), 405 (4.31). Anal. Calcd for C₁₄H₁₁NO₆S₂: C, 47.60; H, 3.14; N, 3.90. Found: C, 47.49; H, 3.19; N, 3.78.

Reaction of Diester Nitrosofulvene 18 with Triphenylphosphine. To a refluxing solution of diester nitrosofulvene 18 (1.0 g) in acetonitrile (20 mL) under nitrogen was added triphenylphosphine (0.90 g). The mixture was refluxed for 3 h more. The solvent was removed and the residue was subjected to chromatography on silica eluted successively with benzene-cyclohexane (1:1), benzene-cyclohexane (7:3), and benzene. Distillation of the residue from the colorless eluant yielded benzonitrile (0.15 g; IR spectrum identical with an authentic sample). The residue from the benzene eluant furnished, after crystallization from methanol, tetraester 22: 0.07 g; mp 165 °C (lit.¹² mp 165 °C); identical with an authentic sample (melting point, mixture melting point, and IR spectrum).

Reaction of Diester Nitrosofulvene 18 with Tri-*n*-butylphosphine in the Presence of Cinnamaldehyde. To a

(8) J. R. Bull, E. R. H. Jones, and G. D. Meakins, *J. Chem. Soc.*, 2601 (1965).

(9) M. Sato, N. C. Gonnella, and M. P. Cava, *J. Org. Chem.*, 44, 930 (1979).

(10) R. Raap and R. G. Micetich, *Can. J. Chem.*, 46, 1057 (1968).

(11) A. Shafiee and I. Lalezari, *J. Heterocycl. Chem.*, 10, 11 (1973).

(12) H. D. Hartzler, *J. Am. Chem. Soc.*, 95, 4379 (1973).

mixture of diester nitrosofulvene 18 (0.33 g) and cinnamaldehyde (0.15 g) in acetonitrile was added tri-*n*-butylphosphine (0.40 g). An instantaneous exothermic reaction occurred, leading to a reddish brown solution. After the mixture was warmed 15 min on the steam bath, the solvent was evaporated under vacuum, and the residue was treated with methanol. The resulting vinyllogous fulvene 26 was filtered. The residue from the filtrate was chromatographed (SiO₂/benzene-cyclohexane, 1:1) to yield more fulvene 26. Crystallization yielded a total of 0.07 g (21%) of 26, mp 125 °C (lit.⁹ mp 124–125 °C).

Conversion of Diphenyl Nitrosofulvene 19 into the Vinyllogous Fulvene 28. To a mixture of nitrosofulvene 19 (0.34 g) and cinnamaldehyde (0.13 mL) in dry acetonitrile (5 mL) at room temperature was added cautiously tri-*n*-butylphosphine (0.4 mL). After the initial exothermic reaction subsided, the reaction mixture was warmed on the steam bath. Cautious addition of methanol containing a trace of HCl afforded shiny glistening plates of 28: 0.30 g; mp 206–212 °C. Recrystallization from acetonitrile afforded pure fulvene 28: 0.27 g (80%); mp 215 °C; mass spectrum, *m/e* (relative intensity) 294 (M⁺, 50), UV-vis λ_{max} 256 nm (log ε 4.393), 388 (4.461). Anal. Calcd for C₁₈H₁₄S₂: C, 73.43; H,

4.79; S, 21.78. Found: C, 73.47; H, 4.87; S, 21.71.

Conversion of Diphenyl Nitrosofulvene 19 into Fulvene 27. Diphenyl nitrosofulvene 19 (0.30 g) was reacted with *p*-chlorobenzaldehyde (0.15 g) in acetonitrile (5 mL) with tri-*n*-butylphosphine (0.5 mL) at room temperature. A workup as described above led to the isolation of the (chlorophenyl)fulvene 27: 0.27 g (55%); mp 239 °C. Recrystallization from BuOAc did not alter the melting point: mass spectrum, *m/e* (relative intensity) 303 (M⁺, 50); UV-vis λ_{max} 244 nm (log ε 4.364), 285 (infl, 3.512), 358 (4.350). Anal. Calcd for C₁₈H₁₁ClS₂: C, 63.45; H, 3.66; S, 21.18. Found: C, 63.61; H, 3.70, S, 21.22.

Acknowledgment. This work was supported by grants from the National Science Foundation (CHE 76-83417 and CHE 79-25017).

Registry No. *cis*-8, 40753-17-1; *trans*-8, 40753-18-2; 12, 51225-41-3; 13, 77965-84-5; 17, 77965-85-6; 18, 77965-86-7; 19, 77965-87-8; 21, 77965-88-9; 22, 26314-39-6; 26, 74151-98-7; 27, 51225-62-8; 28, 51225-56-0; cinnamaldehyde, 104-55-2; *p*-chlorobenzaldehyde, 104-88-1.

Selenosulfonation: Boron Trifluoride Catalyzed or Thermal Addition of Selenosulfonates to Olefins. A Novel Regio- and Stereocontrolled Synthesis of Vinyl Sulfones^{1a}

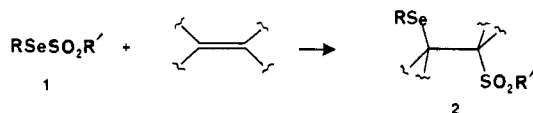
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Received March 9, 1981

Se-Phenyl areneseleosulfonates 1 add to a variety of olefins to produce β-phenylseleno sulfones 2. The reaction may be performed in the presence of boron trifluoride etherate to produce chiefly or exclusively Markovnikov products arising from a stereospecific anti addition. Alternatively, the addition may be thermally induced to afford anti-Markovnikov products generated by a nonstereospecific free-radical process. The two modes of addition achieve complementary regioselectivity. The β-phenylseleno sulfones are converted in high yield to vinyl sulfones by stereospecific oxidation-elimination with *m*-chloroperbenzoic acid.

The additions of selenenyl halides and pseudohalides to olefins have proven to be of both mechanistic interest and synthetic utility in the elaboration of simple unsaturated functionalities.² Although numerous selenenic species have been thoroughly investigated in these and other contexts,³ the selenosulfonates 1 have seldom been

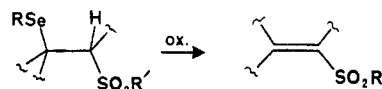


(1) (a) We gratefully acknowledge financial support from the Natural Sciences and Engineering Research Council of Canada and the Research Corp. (b) Recipient of an NSERC Postgraduate Scholarship.

(2) For a review, see: Schmid, G. H.; Garratt, D. G. "The Chemistry of Double-bonded Functional Groups"; Patai, S., Ed., Wiley: London, 1977; Part 2, Chapter 9.

(3) See inter alia: (a) Garratt, D. G.; Kabo, A. *Can. J. Chem.* 1980, 58, 1030. (b) Garratt, D. G.; Ryan, M. D.; Ujjainwalla, M. *Ibid.* 1979, 57, 2145. (c) Garratt, D. G. *Ibid.* 1979, 57, 2180. (d) Clive, D. L. J.; Russell, C. G.; Chittattu, G.; Singh, A. *Tetrahedron* 1980, 36, 1399. (e) Toshimitsu, A.; Aoi, T.; Uemura, S.; Okano, M. *J. Org. Chem.* 1980, 45, 1953. (f) Nicolau, K. C.; Seitz, S. P.; Sipio, W. J.; Blount, J. F. *J. Am. Chem. Soc.* 1979, 101, 3884. (g) Shimizu, M.; Takeda, R.; Kuwajima, I. *Tetrahedron Lett.* 1979, 3461. (h) Denis, J. N.; Vicens, J.; Krief, A. *Ibid.* 1979, 2697. (i) Labar, D.; Krief, A.; Hevesi, L. *Ibid.* 1978, 3967. (j) Hori, T.; Sharpless, K. B. *J. Org. Chem.* 1978, 43, 1689. (k) Reich, H. J.; Wollowitz, S.; Trend, J. E.; Chow, F.; Wendelborn, D. F. *Ibid.* 1978, 43, 1697. (l) Barton, D. H. R.; Britten-Kelly, M. R.; Ferreira, D. *J. Chem. Soc., Perkin Trans. 1* 1978, 1090. (m) McManus, S. P.; Lam, D. H. *J. Org. Chem.* 1978, 43, 650. (n) Raucher, S.; Hansen, M. R.; Colter, M. A. *Ibid.* 1978, 43, 4885. (o) Takahashi, T.; Nagashima, H.; Tsuji, J. *Tetrahedron Lett.* 1978, 799. (p) Liotta, D.; Zima, G. *Ibid.* 1978, 4977.

studied.⁴ It occurred to us that these compounds might also function as selenenylating agents as the sulfinate anion represents a reasonably effective leaving group. We envisaged that the addition of selenosulfonates to olefins would afford β-seleno sulfones 2, thus providing a unique and convenient method for introducing the two synthetically versatile functionalities, sulfone and selenide, into a given unsaturated substrate in one step. Initial experiments revealed that such additions are feasible at room temperature in the presence of boron trifluoride etherate or at elevated temperatures in its absence.⁵ We now report details of our attempts to extend the scope and to elucidate the mechanism of this novel process, which we have named "selenosulfonation". We also describe the facile oxidation-elimination⁶ of β-seleno sulfones to provide a new, efficient route to vinyl sulfones, a class of compounds of proven value in synthesis.⁷



(4) (a) Gancarz, R. A.; Kice, J. L. *Tetrahedron Lett.* 1980, 21, 1697. (b) Austad, T. *Acta Chem. Scand., Ser. A* 1976, A30, 479. (c) Foss, O. *J. Am. Chem. Soc.* 1947, 69, 2236.

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(6) The oxidation-elimination of selenoxides has been reviewed: (a) Reich, H. J. *Acc. Chem. Res.* 1979, 12, 22. (b) Clive, D. L. *J. Tetrahedron* 1978, 34, 1049. (c) Sharpless, K. B.; Gordon, K. M.; Lauer, R. F.; Patrick, D. W.; Singer, S. P.; Young, M. W. *Chem. Scr.* 1975, 8A, 9.