ture of *E*:*Z* isomers (see Table I). The corresponding 1-chloro and 1-iodo compounds were prepared in a similar manner by using *N*-chlorosuccinimide and *N*-iodosuccinimide, respectively.

Thus we have demonstrated that 1-halo-1-(trimethylsilyl)-2,2-dialkyl olefins can be prepared in good yield with high stereoselectivity by carbometalation of alkynylsilanes with dialkylaluminum chlorides–titanocene dichloride followed by carbon–metal bond cleavage with *N*-halosuccinimides.

Experimental Section

Boiling points were recorded at gauge pressure and are reported uncorrected. Infrared spectra were obtained on a Beckman IR-8 spectrometer with only selected absorptions being reported. Nuclear magnetic resonance (^{1}H) spectra were obtained on a Varian EM 390 instrument; chemical shifts are reported as δ values downfield relative to the trimethyl absorption of the silicon-containing compound. High-resolution mass spectra were determined by Mr. Kei Miyano on a Varian M-60 mass spectrometer. Analytical GLC was performed on a F & M research chromatograph Model 810 with either a 50-m SE-30 or 50-m SE-54 glass capillary column.

Diethylaluminum chloride (Texas Alkyls) was used as a neat liquid and assumed to be 7.6 M. Titanocene dichloride (Alfa Products), the *N*-halosuccinimides, and dichloromethane (Mallinckrodt) were used as received. All reactions were stirred magnetically and carried out under an atmosphere of nitrogen in oven-dried (150 °C) glassware.

General Procedure for Preparation of 1-Halo-1-(trimethylsilyl)-2,2-dialkyl Olefins (Table I). In a three-necked, round-bottomed flask that was fitted with two addition funnels, a low-temperature thermometer, a nitrogen adapter, and a magnetic stirring bar was suspended titanocene dichloride (1.1 equiv) in dichloromethane (2 mL/mmol) at room temperature. Addition of diethylaluminum chloride (1.1 equiv) gave a dark-green solution to which was added the alkynylsilane (1 equiv). The resulting dark-red solution was stirred at room temperature for 6 h and then cooled to −78 °C and diluted with dichloromethane (2 mL/mmol of RC≡CSiMe₃). Dry *N*-halosuccinimide (2 equiv) was added at a rate so that the temperature remained below −78 °C (2 h for ~60 mmol of RC≡CSiMe₃) and the mixture was stirred an additional 0.5 h at −78 °C. The resultant red-orange suspension was poured into hexane and washed with an ice cold sodium sulfite–3 N sodium hydroxide mixture. The solids were removed by filtration, and the filtrate was washed with sodium sulfite solution, 3 N hydrochloric acid, and saturated sodium bicarbonate solution and dried over anhdrous sodium sulfate. After removal of the solvent the crude product could be purified either by distillation at reduced pressure in the presence of solid sodium carbonate or by chromatography on silica gel.

(a) (*E*)-1-Bromo-2-ethyl-1-(trimethylsilyl)-1-hexene (4; R = *n*-Bu, X = Br). Following the general procedure, 1-(trimethylsily)-1-hexyne (9.5 g, 61.7 mmol) was reacted with *N*-bromosuccinimide to give 14.6 g (90% distilled yield) of the desired product as a colorless liquid: bp 54–56 °C (0.2 torr); IR (neat) 2960 (s), 2890 (m), 1591 (m), 1455 (s), 1250 (s), 840 (s), 670 (m) cm⁻¹; NMR (CCl₄) δ 0.00 (s, 9 H, (CH₃)₃Si), 0.70 (m, 6 H, 2 CH₃), 1.12 (m, 4 H, CH₂), 2.10 (m, 4 H, 2 —CH₂C≡C); high-resolution mass spectrum,[9] calcd *m/e* for C₁₁H₂₃⁷⁹BrSi 262.0753, found 262.0782.

(b) (*E*)-1-Chloro-2-ethyl-1-(trimethylsilyl)-1-hexene (4; R = *n*-Bu, X = Cl). Following the general procedure, 1-(trimethylsilyl)-1-hexyne (0.924 g, 6.0 mmol) was reacted with *N*-chlorosuccinimide to give 1.114 g (85% chromatographed yield, eluted from 30 g of silica gel with 100% hexane) of the desired product as a colorless liquid: IR (neat) 2960 (s), 2890 (m), 1595 (m), 1455 (s), 1250 (s), 840 (s) cm⁻¹; NMR (CCl₄) δ 0.00 (s, 9 H, (CH₃)₃Si), 0.70 (m, 6 H, 2 CH₃), 1.12 (m, 4 H, CH₂), 2.00 (m, 4 H, 2 —CH₂C≡C); high-resolution mass spectrum,[9] calcd *m/e* for C₁₁H₂₃³⁵ClSi 218.1259, found 218.1252.

(c) (*E*)-2-Ethyl-1-iodo-1-(trimethylsilyl)-1-hexene (4; R = *n*-Bu, X = I). Following the general procedure, 1-(trimethylsilyl)-1-hexyne (0.924 g, 6 mmol) was reacted with *N*-iodosuccinimide to give 1.60 g (86% chromatographed yield, eluted from 30 g of silica gel with 100% hexane) of the desired product as a colorless liquid: IR (neat) 2960 (s), 2890 (m), 1585 (m), 1455 (s), 1250 (s), 840 (s) cm⁻¹; NMR (CCl₄) δ 0.00 (s, 9 H, (CH₃)₃Si), 0.70 (m, 6 H, 2 CH₃), 1.12 (m, 4 H, CH₂), 2.5 (m, 4 H, 2 —CH₂C≡C); high-resolution mass spectrum,[9] calcd *m/e* for C₁₁H₂₃ISi 310.0615, found 310.0637.

(d) (*E*)-1-Bromo-2-cyclohexyl-1-(trimethylsilyl)-1-butene (4; R = cyclohexyl, X = Br). Following the general procedure, cyclohexyl(trimethylsilyl)acetylene[7] (7.00 g, 38.9 mmol) was reacted with *N*-bromosuccinimide to give 8.99 g (80% distilled yield) of the desired product as a colorless liquid: bp 91–92 °C (0.3 torr); IR (neat) 2950 (s), 2880 (m), 1585 (m), 1450 (m), 1250 (s), 885 (s), 845 (s), 760 (m) cm⁻¹; NMR (CCl₄) δ 0.00 (s, 9 H, (CH₃)₃Si), 0.78 (t, 3 H, *J* = 7.5 Hz, CH₃), 0.81–1.65 (m, 10 H), 1.97 (q, 2 H, *J* = 7.5 Hz, —CH₂C≡C), 2.24 (br, 1 H, CHC≡C); high-resolution mass spectrum,[9] calcd *m/e* for C₁₃H₂₅⁷⁹BrSi 288.0910, found 288.0919.

Registry No. 4 (R = *n*-Bu, X = Br), 88315-73-5; 4 (R = *n*-Bu, X = Cl), 88315-74-6; 4 (R = *n*-Bu, X = I), 88315-75-7; 4 (R = C₆H₁₁, X = Br), 88315-76-8; *n*-BuC≡CSiMe₃, 3844-94-8; C₆H₁₁C≡CSiMe₃, 66270-60-8.


Novel Oxidative Rearrangement of *o*-Xylene-α,α′-diylidenebis(4,5-dicarbomethoxy-1,3-dithiole)

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The synthesis and properties of tetrathiafulvalenes have been the subject of much study during the past decade due to the ability of many of these compounds to undergo one-electron oxidation to stable cation radicals which can form the cationic portion of crystalline salts of considerable electrical conductivity.[1,2]

(1) Narita, M.; Pittman, C. U., Jr. *Synthesis*, **1976**, 489.
(2) Engler, E. M. CHEMTECH **1976**, 274.

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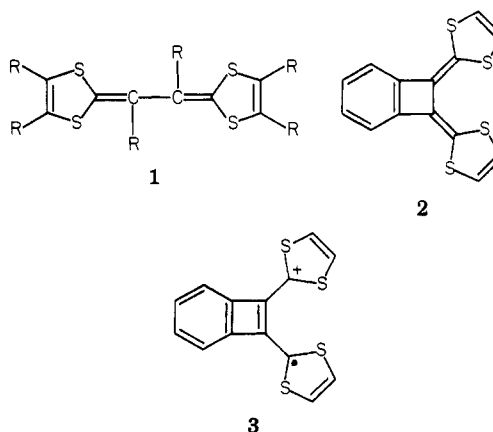
(9) All samples on which high-resolution mass spectral data were obtained were shown to be one peak on a 50-m SE-30 glass capillary column.

In contrast, little is known concerning the chemistry of vinylogous tetrathiafulvalenes of the general structure 1.[3] A particularly interesting example of this type is the benzocyclobutene-derived molecule 2, oxidation of which should generate the unusual cyclobutadienoid cation radical 3.

It has been known for some time that oxidation of the diphenyldithiafulvene 4 affords the dimeric dication 5 by
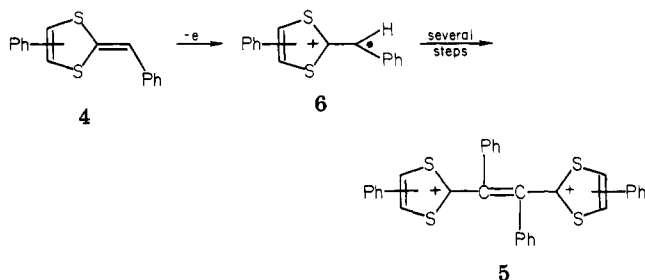
a process involving, as its initial steps, generation and coupling of the unstable cation radical 6.[4] We felt that mild oxidation of o-xylene-α,α'-diylidenebis(4,5-dicarbomethoxy-1,3-dithiole) (7) would take a similar course and lead to the formation of the desired bisfulvene 8, a potential precursor of 3.

The required substrate, o-xylene-α,α'-diylidenebis(4,5-dicarbomethoxy-1,3-dithiole) (7) was synthesized in good yield via the Wittig reaction of o-phthalaldehyde with the phosphorane 9.[5]
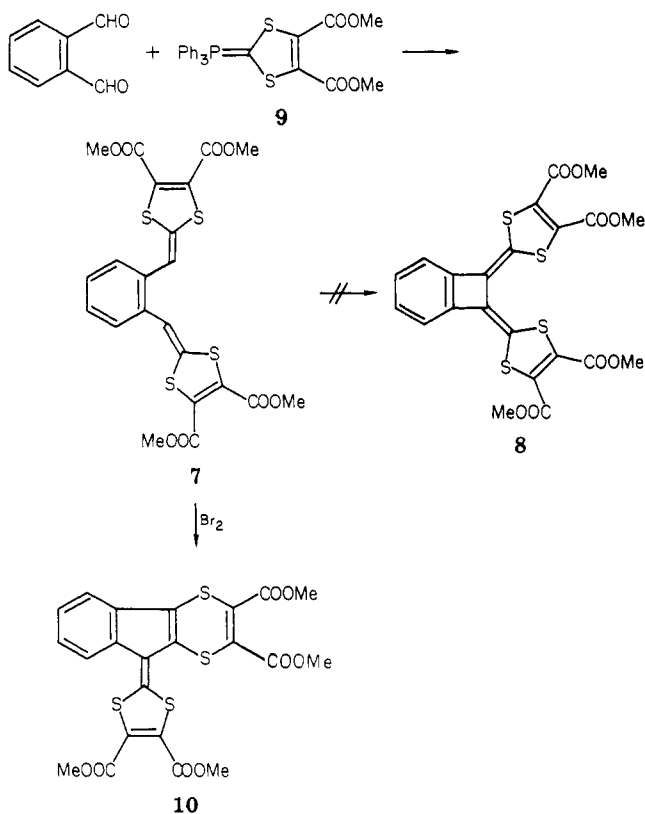
Scheme I. Plausible Mechanisms for the Rearrangement of 7 to 10

E = COOMe
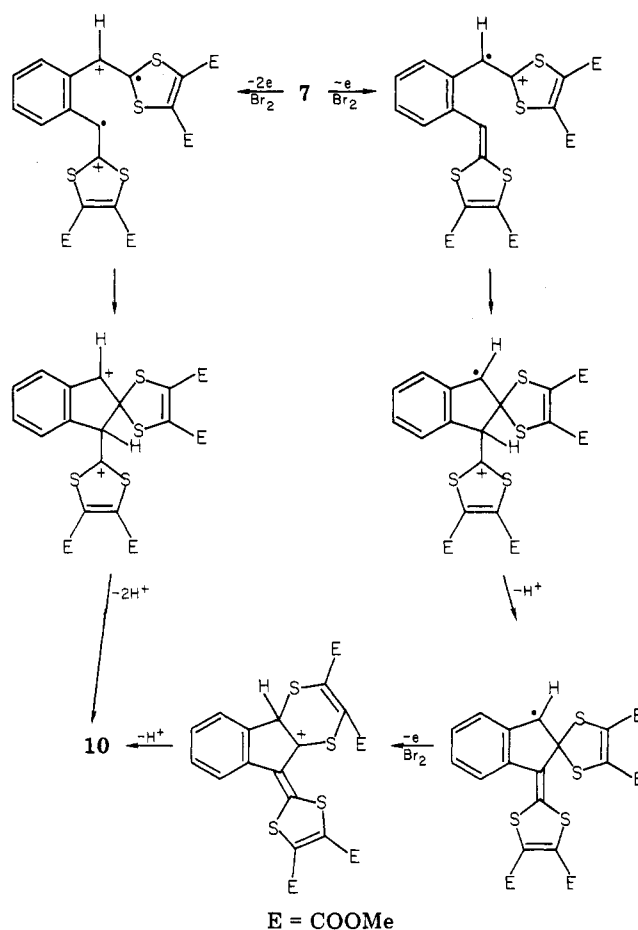
Tetraester 7 reacted with 1 molar equiv of bromine in carbon tetrachloride solution to give a highly crystalline product 10 in 93.3% yield. Electron-impact mass spectral analysis of product 10 showed an apparent molecular ion at m/e 504 (100%) corresponding to $C_{22}H_{16}O_8S_3$, implying loss of one sulfur atom and two hydrogen atoms from tetraester 7 ($C_{22}H_{18}O_8S_4$), and no incorporation of bromine. The chemical ionization mass spectrum of tetraester 9 showed a peak at m/e 536 (15%). The ready loss of sulfur from tetraester 10 upon electron impact was in character with the dithiin structure in the molecule, arising probably out of an unexpected molecular rearrangement. Structure 10 was confirmed by single-crystal X-ray analysis.[6]

While several explanations can be offered for this unusual rearrangement, Scheme I depicts plausible pathways based on our observation of the propensity of simple dithiofulvenes to react readily with radical reagents.

Experimental Section

General Methods. Melting points were determined on a Thomas-Hoover apparatus and are uncorrected. Electron-impact

(3) Cava, M. P.; Lakshmikantham, M. V. J. Heterocycl. Chem. 1980, 17, S-39. Recently two new vinylogues of TTF have been synthesized: (a) Yoshida, Z.; Kawase, T.; Awaji, H.; Sugimoto, I.; Sugimoto, T.; Yoneda, S. Tetrahedron Lett. 1983, 24, 3469. (b) Yoshida, Z.; Kawase, T.; Awaji, H.; Yoneda, S. Ibid. 1983, 24, 3473.
(4) Kirmse, W.; Horner, L. Liebigs Ann. Chem. 1958, 614, 4.
(5) Sato, M.; Gonnella, N. C.; Cava, M. P. J. Org. Chem. 1979, 44, 930.

and chemical ionization mass spectra were determined on a VG Micromass 7070 H machine. UV–vis spectra were determined in MeCN solution on a Perkin-Elmer 202 spectrometer. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

o-**Xylene-α,α′-diylidenebis(4,5-dicarbomethoxy-1,3-dithiole) (7).** To a stirred mixture of (4,5-dicarbomethoxy)thiolyl triphenyl phosphonium fluoborate[5] (10.5 g) and *o*-phthalaldehyde (1 g) in dry acetonitrile (100 mL) under argon was added excess Et$_3$N (10 mL). After 4–5 h of stirring under argon, the mixture was diluted carefully with water until no more crystals precipitated. The crystalline product was filtered, washed with water and methanol successively, and dried to give crude tetraester 7, mp, 130 °C with prior shrinking at 114 °C (3.7 g, 92%); an analytical sample was obtained by recrystallization from methanol–methylene chloride and had mp 130 °C; mass spectrum, *m/e* 538 (14%): UV–vis spectrum λ$_{max}$ 235 nm (log ε 4.083), 310 sh (4.106), 365 (4.208). Anal. Calcd for C$_{22}$H$_{18}$O$_8$S$_4$: C, 49.05; H, 3.37; S, 23.82. Found: C, 49.01; H, 3.50; S, 26.05.

Dithiino Fulvene Tetraester (10). To a solution of bisfulvene tetraester 7 (1.076 g) in CCl$_4$ (10 mL) under argon was added a solution of Br$_2$ (0.32 g) in CCl$_4$ (4 mL). Upon stirring at room temperature, HBr evolved and it was observed that light increased the rate of HBr evolution. After HBr evolution slackened, the dark solution was filtered through a short column of alumina, and the eluant was evaporated in vacuo. The crystalline residue (1 g) was recrystallized from benzene to give very dark red rhombs of tetraester 10: mp 198 °C (0.85 g; 79.3%); mass spectrum (EI), *m/e* 504 (100%) (CI) 536 (15%); UV–vis spectrum, λ$_{max}$ 235 nm (log ε 4.221), 258 br (4.253), 300 sh (3.855), 400 (4.309). Anal. Calcd for C$_{22}$H$_{16}$O$_8$S$_4$: C, 49.24; H, 3.00; S, 23.90. Found: C, 49.49; H, 3.06; S, 23.7.

Supplementary Material Available: Full X-ray data for compound 10 (5 pages). Ordering information is given on any current masthead page.

Communications

Two New Asymmetric Epoxidation Catalysts. Unusual Stoichiometry and Inverse Enantiofacial Selection

Summary: Use of TiCl$_2$(O-*i*-Pr)$_2$ instead of Ti(O-*i*-Pr)$_4$ with tartrate diesters (in a 2:1 ratio) affords the chloro diols arising from regiospecific opening of intermediate epoxides of *opposite* enantioselectivity to those produced in the standard asymmetric epoxidation. These "inverse" epoxides are also obtained in oxidations catalyzed by Ti(O-*i*-Pr)$_4$ and tartramide ligands in the 2:1 ratio.

Sir: We have recently reported evidence for the dimeric nature of the standard (2:2) titanium–tartrate asymmetric epoxidation catalysts.[1] During the past several months we have discovered three new asymmetric catalyst systems that depend on a titanium to tartrate ligand ratio of 2:1.[2] Furthermore, the two systems that involve epoxidation of an allylic alcohol effect this transformation with an enantiofacial selection that is opposite to that of the standard catalyst. These two systems are the subject of this report.

Tartramide Ligands. The first of these new systems evolved from work that began at Stanford on modified tartrate ligands. Initially, erratic results were obtained

Table I.   Epoxidation of (*E*)-α-Phenylcinnamyl Alcohol with Various 2:1 Ti(O-*i*-Pr)$_4$–Tartramide Complexes

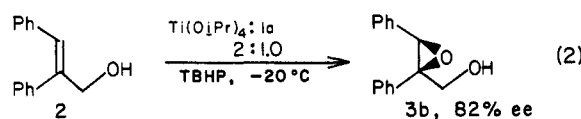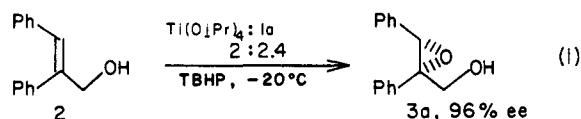| (+)-tartramide	epoxy alcohol,[a] % ee (2R, 3R)
1b	84
1c	53
1d	66

[a] Enantiomeric excess (ee) determined by HPLC on two ionically bound Pirkle type 1-A column in series (Regis Chemical Co. Hi-Chrom reversible HPLC column).

with the amides derived from tartaric acid,[3] but careful reinvestigation of amide ligands such as 1a has led to the

1a , R^1 = R^2 = NHCH$_2$Ph
1b , R^1 = NHCH$_2$Ph , R^2 = N◁
1c , R^1 = R^2 = N◁
1d , R^1 = R^2 = NHCH$_2$CH$_2$CH$_3$
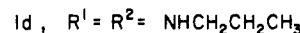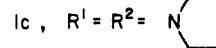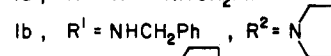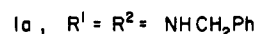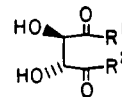
remarkable discovery revealed in eq 1 and 2.

(1) (a) Sharpless, K. B.; Woodard, S. S.; Finn, M. G. *Pure Appl. Chem.* 1984, 55, 1823–1836. (b) The standard asymmetric epoxidation conditions include the use of slightly greater than 1 equiv of tartrate per equiv of Ti.[18] We denote this sytem as "2:2", however, because it is the complex with the 2:2 Ti:tartrate stoichiometry that is the active catalyst under these conditions.

(2) (a) Miyano, S.; Lu, L. D.; Viti, S. M.; Sharpless, K. B. *J. Org. Chem.* 1983, 48, 3608–3611. (b) Hill, J. G.; Rossiter, B. E.; Sharpless, K. B. *Ibid.* 1983, 48, 3607–3608. (c) Altering the titanium–tartrate ratio in the opposite direction (i.e., Ti:tartrate = 2:4) gives an effective reagent for the asymmetric oxidation of certain sulfides (H. B. Kagan and P. Pitchen, private communication). We had earlier shown that the 2:4 Ti:tartrate species is completely inactive as an epoxidation catalyst for allylic alcohols (Woodard, S. S. Ph.D. Dissertation, Stanford University, Stanford, CA, 1981).

(3) Zilenovsky, J.; Sharpless, K. B., unpublished results.