for 191 variables, and the maximum residual density was 0.25 e $Å^{-3}$.

Acknowledgment. We thank the Italian Ministry of Education (MPI funds) for partial support of this work.

Supplementary Material Available: Tables of coordinates for hydrogen atoms, anisotropic thermal parameters, bond distances and angles, torsion angles, and least-squares planes for macrocycle **16d** (6 pages). Ordering information is given on any current masthead page.

Some Transformations of 2-Methylene-1,3-diselenoles

M. V. Lakshmikantham,* Yvette A. Jackson, and Michael P. Cava*

Department of Chemistry, University of Alabama, P.O. Box H, Tuscaloosa, Alabama 35487-9671

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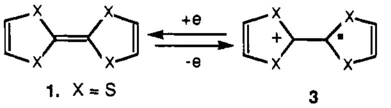
2-Benzylidene-4-phenyl-1,3-diselenole (**5**) was transformed into the green nitroso derivative **7** and the red phenylazo derivative **8** by reaction with NO^+ and PhN_2^+ ions, respectively. Although the parent heterocycle **10** failed to give such substitution and underwent extensive decomposition, it could be transformed into the formyl derivative **13** as well as the novel push–pull-stabilized thioaldehyde **15**. Formyl derivative **13** was further converted into the vinylogous π-donor **20** in ~50% yield. Several other reactions of aldehyde **13** are also reported.

There has been considerable interest in the chemistry of tetrathiafulvalene (**1**, TTF) and its selenium analogue (**2**, TSeF) as a result of the ability of these compounds and many of their derivatives to undergo reversible one-electron oxidation leading to stable cation radicals (**3**), many salts of which show unusual electrical conductivity in the solid state.[1]

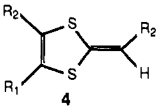


1. X = S

2. X = Se

3

Some years ago, we reported a number of novel reactions of several 2-(substituted methylene)-1,3-dithioles (**4**; 1,4-dithiafulvenes),[2] compounds that represent partial structural analogues of tetrathiafulvalenes.[2] In this paper, we present the results of a study of some transformations of the analogous 5-phenyl-2-(phenylmethylene)-1,3-diselenole (**5**)[3] as well as of the parent heterocycle **10**.[4]



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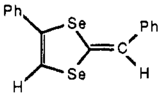

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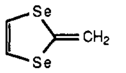


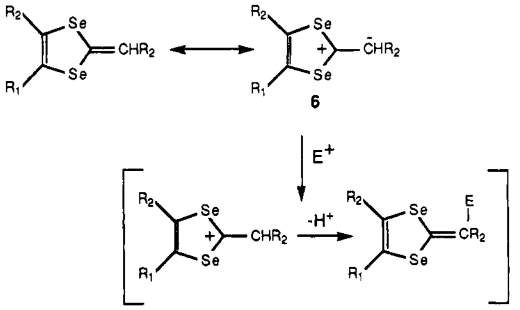
10

Results and Discussion

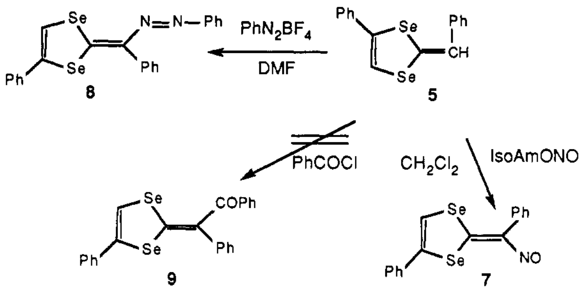
Reactions at the Exo Methylene Position. In view of the presumed importance of the dipolar contributor **6** (Scheme I), electrophilic substitution at the exocyclic carbon might at first be expected, although substitution by an electron-transfer process would be more analogous to the behavior of the corresponding dithiafulvene system.[2]

Our initial investigations were carried out with readily available *cis*-5-phenyl-2-(phenylmethylene)-1,3-diselenole (**5**).[3] The corresponding trans isomer afforded the same products.[5] Diselenole **5** was substituted readily by nitrosonium and benzenediazonium ions to yield products **7** and **8**, whereas the use of benzoyl chloride did not lead to **9**, but led to recovery of isomerized starting material (Scheme II). This behavior paralleled that of the corresponding sulfur analogue **4** (R_1 = H, R_2 = Ph), and strengthened our belief that perhaps the reactions were occurring via electron transfer rather than by electrophilic substitution.

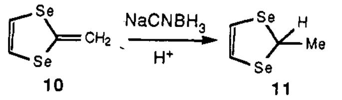
Scheme I



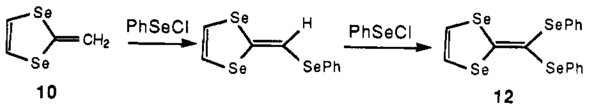
Scheme II



Scheme III



Scheme IV



In a recent publication, we described the preparation of the parent 2-methylene-1,3-diselenole (**10**) and its oxidative conversion by iodine to TSeF (**2**).[4] In contrast to the behavior of **5**, diselenole **10** did not give characterizable

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[1] Bryce, M. R. *Aldrichim. Acta* **1985**, *18*, 73 and references cited therein.

[2] Lakshmikantham, M. V.; Cava, M. P. *J. Org. Chem.* **1981**, *46*, 3246.

[3] Lalezari, I.; Shafiee, A.; Yalpani, M. *J. Org. Chem.* **1973**, *38*, 338.

[4] Jackson, Y. A.; White, C. L.; Lakshmikantham, M. V.; Cava, M. P. *Tetrahedron Lett.* **1987**, *28*, 5635.

[5] This assignment is arbitrary and is based on the known chemistry of **5** isomerizing quantitatively to the *trans*-diphenyl compound in the presence of a trace of acid (see ref 3).

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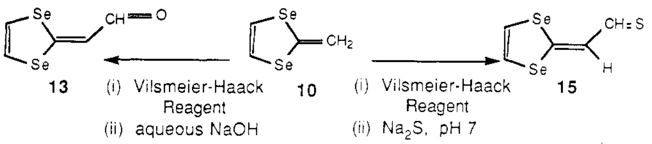
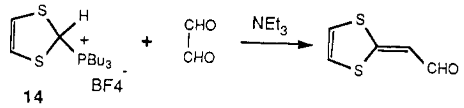
Scheme V



Scheme VI



substitution products with nitrosonium or phenyldiazonium reagents, although it underwent extensive decomposition. This was not surprising in view of the fact that diselenole **10**, in contrast to **5**, was stable for only about 2 weeks, even when stored under nitrogen in the freezer.

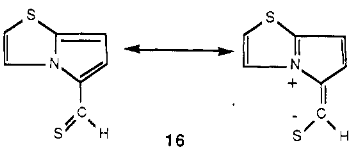
The exocyclic methylene of **10** is readily protonated to give a highly reactive 1,3-diselenonium ion,[6] which immediately attacks unchanged **10** to give polymeric material. In the presence of sodium cyanoborohydride, the diselenonium ion is intercepted to give 2-methyl-1,3-diselenole **11** (Scheme III).

Whereas **10** could not be benzoylated at the exo methylene carbon, it could be disubstituted by using 2 equiv of phenylselenenyl chloride in the presence of pyridine to give **12** in 33% yield. Attempts to isolate the monoselenated intermediate were unsuccessful (Scheme IV).

2-Methylene-1,3-diselenole reacted smoothly with the Vilsmeier–Haack reagent (phosphoryl chloride in dimethylformamide) followed by treatment with aqueous hydroxide to yield 2-(formylmethylene)-1,3-diselenole (**13**) as yellow crystals in 60–65% yield (Scheme V).

Although the phenylselenenyl cation and the Vilsmeier reagent generally function as ionic electrophiles, both species are capable of adding one electron to give stabilized radicals. Hence, their reactions with **10** may be further examples of electron-transfer substitution in this system.

The sulfur analogue of aldehyde **13** was prepared by Yoshida et al. by reacting 1,3-dithiolyl-2-tributylphosphonium tetrafluoroborate (**14**) with glyoxal in the presence of triethylamine[7] (scheme VI). In view of the fact that the selenium analogue of **14** is unknown, our method offers the only route at present to 2-(formylmethylene)-1,3-diselenole (**13**).



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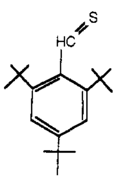

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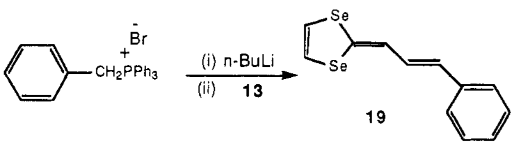
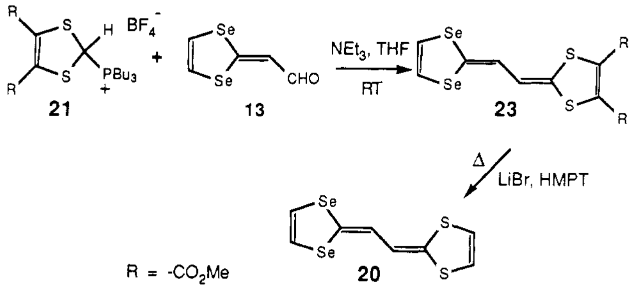
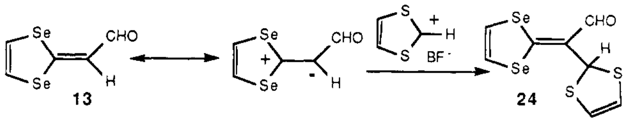
Scheme VII



Scheme VIII



Scheme IX



Treatment of the Vilsmeier–Haack reaction intermediate derived from **10** with buffered sodium sulfide solution led to the formation of the remarkably stable bronze-colored thioaldehyde **15** (Scheme V). Attempts to synthesize thioaldehydes generally have led to cyclic or linear polymers due to the opening of the C=S bond, except in special cases that allow for stabilization of the thione function by electron donation or steric bulk. Examples of such cases are compounds **16** and **17**.[8,9] In the case of aldehyde **15** an alternate closed form **18** is conceivable, by analogy to the stable thiathiophthene system.[10] The ^{1}H NMR and ^{13}C NMR spectra of **15** rule out this possibility. The thioformyl proton resonance occurs at δ 10.83 as a doublet with J = 7 Hz; the carbon resonance of the thioformyl group occurs at 195.8 ppm, a value further downfield from that shown by the corresponding aldehyde **13** at 181.8 ppm. The olefinic carbon adjacent to sulfur in structure **18** would, on the other hand, be expected to appear at higher field than the aldehyde carbonyl.

18

Transformations of 2-(Formylmethylene)-1,3-diselenole (13). Aldehyde **13** readily underwent a Wittig reaction with the ylide from benzyltriphenylphosphonium bromide to produce the new fulvene vinylogue **19** in 55% yield after 4 h at room temperature (Scheme VII).

The reactivity of aldehyde **13** with phosphoranes was further exploited for a convenient synthesis of ethanediylidene-2-(1,3-dithiole)-2′-(1,3-diselenole) (**20**). A different synthesis of this unusual donor compound has been reported previously by Yoshida et al. starting from the costly carbon diselenide via four steps.[11]

Our synthesis of the vinylogous dithiadiselenafulvalene **20** was achieved as outlined in Scheme VIII. The phosphonium salt **21**[13] reacted with aldehyde **13** in the presence of triethylamine at room temperature to give diester **23**, which was then decarbomethoxylated in the usual manner to produce ethanediylidene-2-(1,3-dithiol)-2′-(1,3-diselenole) (**20**).

The properties of **20** were in total agreement with those reported by Yoshida et al.[11]

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(6) Engler, E. M.; Patel, V. V. *Tetrahedron Lett.* **1975**, 1259.

(7) Yoshida, Z. I.; Kawase, T.; Awaji, H.; Sugimoto, I. *Tetrahedron Lett.* **1983**, *24*, 3469.

(8) Mackie, R. K.; Mckenzie, S.; Reid, D. H.; Webster, R. G. *J. Chem. Soc., Perkin Trans. 1* **1973**, 657.

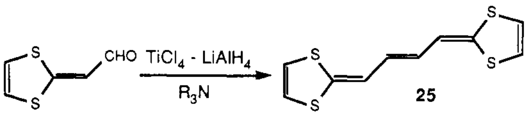
(9) Okazaki, R.; Ishii, A.; Fukuda, N.; Oyama, M.; Inamoto, M. *J. Chem. Soc., Chem. Commun.* **1982**, 1187.

(10) Davy, H.; Vialle, J. *Bull. Soc. Chim. Fr.* **1975**, 1435.

(11) Yoshida, Z. I.; Awaji, H.; Sugimoto, T. *Tetrahedron Lett.* **1984**, *25*, 4227.

2-(Formylmethylene)-1,3-diselenole underwent an unusual reaction with 1,3-dithiolium tetrafluoroborate in THF solution to yield the new aldehyde **24**, as evidenced by NMR, IR, and MS (Scheme IX).

Yoshida et al. reported that 2-(formylmethylene)-1,3-dithiole underwent reductive coupling with $TiCl_4$–$LiAlH_4$ to give the vinylogous TTF **25**.[12] In contrast, attempts to deoxygenate aldehyde **13** using $TiCl_4$–$LiAlH_4$ have been unsuccessful.



Experimental Section

General. All melting points are uncorrected and were determined on a Thomas-Hoover melting point apparatus. Ultraviolet–visible, IR (KBr), mass, and ^1H NMR spectra were determined on Perkin-Elmer 4, Perkin-Elmer 781, Finnigan, and Bruker 90-MHz spectrometers, respectively. ^{13}C NMR spectra were determined on a 200-MHz Nicolet instrument. All NMR spectra were done in $CDCl_3$ solution, and δ values are reported in ppm downfield from TMS. Elemental analyses (C, H, N, S) were carried out by Atlantic Microlabs, Atlanta, GA. Selenium analyses were done by Galbraith Labs, Knoxville, TN.

5-Phenyl-2-(nitrosophenylmethylene)-1,3-diselenole (7). To a solution of 5-phenyl-2-(phenylmethylene)-1,3-diselenole[3] (**5**, 1 g) in methylene chloride (25 mL) at room temperature was added excess isoamyl nitrite (0.5 g). The dark green mixture was left aside for 3 h and the shiny green crystals were filtered. Recrystallization from CH_2Cl_2–MeOH gave dark green crystals, mp 200 °C (dec). The yield was 0.8 g (74.1%); mass spectrum, *m/e* (relative intensity) 393 (4, M$^+$), 363 (8, M– NO), 182 (15), 102 (100); ^1H NMR spectrum, δ 8.20, 8.10 (s, 1 H), 7.92–7.85 (m, 2 H), 7.63–7.46 (m, 8 H); UV–visible spectrum, λ_{max}^{MeCN} 230 nm, sh (ϵ 21 176), 245 (22 745), 278 sh (16 470), 448 (16 470). Anal. Calcd for $C_{16}H_{11}NOSe_2 \cdot CH_3OH$: C, 48.24; H, 3.57; N, 3.31. Found: C, 48.09; H, 2.89; N, 3.49.

5-Phenyl-2-((phenyldiazo)phenylmethylene)-1,3-diselenole (8). To a suspension of **5** (182 mg)[3] in acetonitrile (5 mL) was added phenyldiazonium fluoborate (100 mg). The color turned violet instantaneously. Dilution with water and standard workup followed by chromatography yielded azo compound **8** (120 mg, 51%) after crystallization from methanol as red fluffy needles, mp 170–175 °C; mass spectrum, *m/e* (relative intensity) 469 (13, M$^+$), 364 (38, M– PhN_2), 182 (15), 169 (38), 102 (85), 77 (100); ^1H NMR spectrum, δ 7.9–7.75 (m, 3 H), 7.55–7.30 (m, 13 H); UV–visible spectrum, $\lambda_{max}^{CH_2Cl_2}$ 227.9 nm (ϵ 23 368), 255.4 (26 948), 284 (18 204), 500 (23 888). Anal. Calcd for $C_{22}H_{16}N_2Se_2$: C, 56.67; H, 3.46; N, 6.01. Found: C, 56.14; H, 3.51; N, 5.91.

2-Methyl-1,3-diselenole (11). To a solution of 2-methylene-1,3-diselenole (**10**, 0.75 g)[4] in benzene was added sodium cyanoborohydride (0.3 g) followed by acetic acid (2 mL), containing concentrated sulfuric acid (0.1 mL). The mixture was stirred for an hour. It was then washed with water several times and dried. The residue from the benzene was chromatographed on silica using cyclohexane as eluant to yield **11** as a low-melting solid, mp 30 °C (0.12 g); ^1H NMR spectrum, δ 7.04 (s, 2 H), 5.10 (q, J = 7.5 Hz, 1 H), 1.90 (d, J = 7.5 Hz, 3 H); mass spectrum, *m/e* (relative intensity) 214 (74.9, M$^+$), 201 (30.9), 199 (100), 160 (43.6).

2-(Bis(phenylseleno)methylene)-1,3-diselenole (12). To a chilled solution of 2-methylene-1,3-diselenole (**10**, 0.2 g)[4] in methylene chloride (8 mL) containing pyridine (0.38 mL) was added a solution of phenylselenenyl chloride (0.4 g) in methylene chloride (4 mL). The mixture turned dark and opaque. The mixture was stirred overnight at room temperature and was then filtered and washed successively with dilute hydrochloric acid, water, saturated sodium bicarbonate solution, and water. Removal of solvent followed by chromatography (SiO_2, hexane–benzene (3:1)) yielded **12**, which was crystallized from CH_2Cl_2–MeOH to give tan crystals (165 mg, 33%), mp 120–122 °C; ^1H NMR spectrum, δ 7.21–7.50 (m); mass spectrum, *m/e* (relative intensity) 524 (12, M$^+$), 367 (17.6), 290 (8.7), 181 (50), 77 (100); UV–visible spectrum, $\lambda_{max}^{CH_2Cl_2}$ 228.5 nm (ϵ 21 051), 255.9 sh (14 200), 297 sh (7749), 337 (8800). Anal. Calcd for $C_{16}H_{12}Se_4$: C, 36.95; H, 2.33; Se, 60.72. Found: C, 36.78; H, 2.37; Se, 60.46.

2-(Formylmethylene)-1,3-diselenole (13). Phosphorus oxychloride (0.5 mL) was added to dry DMF (2 mL) at 0 °C. A solution of diselenole **10** (1.0 g) in DMF (2 mL) was added dropwise with swirling. The mixture was kept at room temperature for an hour and then diluted with ice water (180 mL) followed by aqueous sodium hydroxide (40 mL). After an hour, the mixture was cooled, the precipitate was filtered, and the product was purified by column chromatography (SiO_2, benzene) to give yellow crystals (735 mg, 65%). Crystallization from methylene chloride–hexane yielded yellow crystals of **13**, mp 102–103 °C; IR spectrum, 1600 cm^{-1} (>CO); ^1H NMR spectrum δ 9.53 (d, J = 1.6 Hz, 1 H), 7.40 (AB q, J = 8.2 Hz, 2 H), 7.30 (br, 1 H); ^{13}C NMR spectrum, δ 181.8, 128.35, 123.38, 114.56; mass spectrum, *m/e* (relative intensity) 240 (100, M$^+$), 212 (40.3), 160 (35.3), 106 (35.7); UV–visible spectrum, $\lambda_{max}^{CH_2Cl_2}$ 214.8 nm (ϵ 3788), 228.8 (4476), 254.8 (7894), 375.1 sh (12 059), 389.9 (16 588). Anal. Calcd for $C_5H_4OSe_2$: C, 25.23; H, 1.69. Found: C, 25.05; H, 1.60.

2-(Thioformylmethylene)-1,3-diselenole (15). The reaction with the Vilsmeier–Haack reagent (prepared from 1.5 mL of $POCl_3$ and 6 mL of DMF) was carried out as described above on 1,3-diselenole **10** (3.0 g). Decomposition of the intermediate complex was carried out with aqueous sodium sulfide ($Na_2S \cdot 9H_2O$, 15.0 g in 450 mL of water) buffered to pH 7.2 with sodium dihydrogen phosphate. Standard workup yielded practically pure thioaldehyde (2.8 g, 77%). Crystallization from methanol yielded shiny bronze plates of **15**, mp 107–109 °C; IR spectrum, 1210, 1260 cm^{-1} (>CS); ^1H NMR spectrum, δ 10.83 (d, J = 7 Hz, 1 H), 8.54 (d, J = 7 Hz, 1 H), 8.04 (d, J = 7 Hz, 1 H), 7.91 (d, J = 7 Hz, 1 H); ^{13}C NMR spectrum, δ 195.78, 127.95, 127.54, 126.95; mass spectrum, *m/e* (relative intensity) 256 (61, M$^+$), 230 (100), 117 (41.6), 69 (84); UV–visible spectrum, $\lambda_{max}^{CH_2Cl_2}$ 228.5 nm (ϵ 8863), 243.6 (8177), 278.9 (13 265), 465 (21 547). Anal. Calcd for $C_5H_4SSe_2$: C, 23.64; H, 1.59; S, 12.62. Found: C, 23.36; H, 1.53; S, 12.87.

2-(Cinnamylmethylene)-1,3-diselenole (19). To a suspension of benzyltriphenylphosphonium bromide (180 mg) in dry THF (10 mL) at –78 °C was added under nitrogen 2.5 M *n*-butyllithium in hexane (0.17 mL). To the resulting ylide (orange), a solution of aldehyde **13** (100 mg) in THF (8 mL) was added. The mixture was stirred for 4 h at room temperature, and the solvent was evaporated. The residue was extracted into benzene. The benzene extract was evaporated and the residue was purified by column chromatography (SiO_2, benzene–hexane (1:1)) to give yellow crystals (73 mg, 56%) of product **19**. Recrystallization from CH_2Cl_2–MeOH yielded pure **19**, mp 135–137 °C; ^1H NMR spectrum, δ 7.3–7.20 (m, 5 H), 7.13 (s, 2 H), 6.3–6.7 (m, 3 H); mass spectrum, *m/e* (relative intensity) 314 (12.7, M$^+$), 208 (17.5), 128 (100); UV–visible spectrum, $\lambda_{max}^{CH_2Cl_2}$ 215.8 nm (ϵ 12 548), 262.4 (20 887), 378.1 (24 636). Anal. Calcd for $C_{12}H_{10}Se_2$: C, 46.18; H, 3.23. Found: C, 45.88; H, 3.22.

Ethanediylidene-2-(4,5-dicarbomethoxy-1,3-dithiole)-2′-(1,3-diselenole) (23). To a mixture of aldehyde **13** (1.0 g) and excess triethylamine (1.32 g) in THF (5 mL) was added phosphonium salt **21**[13] little by little until no more **13** was present. A total of 3.9 g of **21** was used. The solvent was evaporated and the residue upon trituration with methanol furnished practically pure crystals of **23** (1.17 g, 63%), mp 115 °C. Recrystallization from CH_2Cl_2–hexane gave dark red crystals, mp 120 °C; IR spectrum, 1710 cm^{-1} >CO; ^1H NMR spectrum, δ 7.298 (s, 2 H), 7.146 (s, 2 H), 3.866 (s, 6 H); mass spectrum, *m/e* (relative intensity) 442 (100, M$^+$); UV–visible spectrum, $\lambda_{max}^{CH_2Cl_2}$ 231 nm (ϵ 11 250), 383.3 (18 810), 403 sh (13 942). Anal. Calcd for $C_{12}H_{10}O_4S_2Se_2$: C, 32.74; H, 2.29; S, 14.56. Found: C, 32.82; H, 2.32; S, 14.68.

Ethanediylidene-2-(1,3-dithiole)-2′-(1,3-diselenole) (20). Diester **23** was subjected to decarbomethoxylation with LiBr–HMPT, using a previously published procedure.[14] The vinylogous

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(12) Yoshida, Z. I.; Kawase, T.; Awaji, H.; Yoneda, S. *Tetrahedron Lett.* **1983**, *24*, 3473.

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

fulvene **20** (360 mg) was obtained from diester **23** (0.6 g) in 81% yield. Recrystallization from cyclohexane furnished yellow crystals, mp 165 °C (dec) (reported mp 162 °C (dec)).[11] The spectral (UV-visible, NMR, mass) data for **20** were in agreement with those reported.[11]

2-(Formyl(1,3-dithiol-2-yl)methylene)-1,3-diselenole (24). A mixture of 1,3-dithiolium tetrafluoroborate[15] (100 mg) and aldehyde **13** (100 mg) in THF (10 mL) was stirred at room temperature for 1 h. The solvent was evaporated and the residue was subjected to flash chromatography (SiO_2, benzene) to give product **24** (112 mg, 77%), which was crystallized from methanol to give yellow needles of **24**, mp 138 °C; IR spectrum, 1600 cm^{-1} (>CO); ^1H NMR spectrum, δ 9.55 (s, 1 H), 7.99 (AB q, J = 9 Hz, 2 H), 6.54 (s, 1 H), 6.14 (s, 2 H); mass spectrum, m/e (relative intensity) 342 (98.8), 340 (100), 313 (37.5), 182 (80.6), 103 (76.9); UV-visible spectrum, $\lambda_{max}^{CH_2Cl_2}$ 227.1 nm (ϵ 16768), 251.8 (18431), 395.6 (30034). Anal. Calcd for $C_8H_6OS_2Se_2$: C, 28.10; H, 1.77. Found: C, 28.20; H, 1.79.

Reaction of 2-Benzylidene-4-phenyl-1,3-diselenole (5) with Benzoyl Chloride. A solution of **5** (364 mg) in CH_2Cl_2 (5 mL) was treated with benzoyl chloride (0.12 mL). Shiny yellow plates separated, which were filtered, washed, and dried to give the trans isomer of **5** (330 mg), mp 228 °C, identical (IR, MS, mp) with an authentic sample prepared according to ref 3.

The above reaction was also carried out in the presence of pyridine as solvent (3 mL). The reaction mixture was heated at 100 °C for 2 h. Workup led to the isolation of starting material (200 mg).

Attempted Coupling of Aldehyde 13 with $TiCl_4$-LAH. To a suspension of LAH (4 mg) in dry THF (5 mL) was added via syringe a solution of $TiCl_4$ (0.5 mL) in THF (3 mL). An exothermic reaction ensued, leading to a yellow solution. To this solution was added a mixture of aldehyde **13** (200 mg) and triethylamine (0.12 mL) in dry THF (6 mL). The mixture was refluxed overnight. The cooled reaction mixture was diluted with 20% aqueous K_2CO_3 and extracted with benzene. Evaporation of benzene led to the recovery of starting material.

Attempted Desulfurization of Thioaldehyde 15.[16] A solution of **15** (0.95) and hexabutyldistannane (2.2 mL) in benzene (1.0 L) was photolyzed for 14 h using a medium-pressure lamp. The solvent was evaporated. The residue was extracted with hexane. The residue from the hexane-soluble fraction (2.6 g) was malodorous, and the TLC (SiO_2, $CHCl_3$-hexane (1:1)) was complex. Chromatographic resolution led to the partial purification of the product(s). Two components were identified by mass spectrometry as recovered hexabutyldistannane (0.9 g) and hexabutylditin selenide ($(Bu_3Sn)_2Se$ (0.6 g)).

Acknowledgment. This work was supported by a grant from the National Science Foundation (Grant NSF-86-07458).

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[14] Lakshmikantham, M. V.; Cava, M. P. *J. Org. Chem.* **1976**, *41*, 882.

[15] Wudl, F.; Kaplan, M. L. *J. Org. Chem.* **1974**, *39*, 3608.

[16] This reaction was based on the reported desulfurization of 1,3-dithiole-2-thione by: Ueno, Y.; Nakayana, A.; Okanava, M. *J. Am. Chem. Soc.* **1976**, *98*, 7440.

Anion-Catalyzed Reactions of Silyl Ester Polyenolates with Electrophiles[†]

Walter R. Hertler,* Gade S. Reddy, and Dotsevi Y. Sogah

Central Research and Development Department, E. I. du Pont de Nemours and Co., Inc., Experimental Station, Wilmington, Delaware 19898

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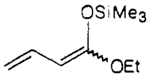
The stereochemical assignments for the trimethylsilyl ester polyenolates **1**, **2**, and **3** have been made. Unlike simple silyl ketene acetals, **1**, **2**, and **3** are obtained predominantly as the thermodynamic *Z* isomers. Bifluoride-catalyzed equilibration studies showed the equilibrium compositions of **1**, **2**, and **3** to be 89% *Z*, 67% *Z*, and 95% 1-*Z*,3-*E*, respectively. The regiochemistry of the bifluoride-catalyzed Reformatsky-type reaction of benzaldehyde with **1**, **2**, and **4** was determined. Regiochemical control of the condensation of **1** with benzaldehyde by reaction temperature was demonstrated, with 95% α reaction at −95 °C and 99% γ-reaction at +34 °C. Mechanism studies are consistent with a dissociative process in which a dienolate reacts with benzaldehyde at the α position to give the kinetic-controlled product, and as the reaction temperature increases, increasing amounts of the thermodynamic γ product are formed. A nondissociative cyclic process leading to α product may occur at low temperatures. The naked ester dienolate prepared by reaction of **1** with TASF and removal of the resulting fluorotrimethylsilane was alkylated by benzyl bromide exclusively at the α position at −100 °C. The bifluoride-catalyzed reverse reaction of **1** with benzaldehyde is much slower than the processes that determine the regiochemistry in the forward reaction.

The importance of development of synthetic methodologies for the formation of carbon–carbon double bonds has stimulated interest by several research groups in studies of carbon–carbon bond-forming reactions of carbon electrophiles with silyl ester polyenolates such as **1** and **2**, lithium ester polyenolates, and dilithium acid polyenolates.[1-13] In general, the regiochemistry of the reactions



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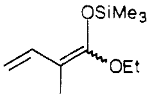

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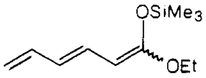

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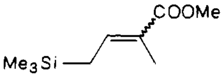

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[†] Contribution no. 4373.

[1] Fleming, I.; Goldhill, J.; Paterson, I. *Tetrahedron Lett.* **1979**, *20*, 3209.

[2] (a) Fleming, I.; Goldhill, J.; Paterson, I. *Tetrahedron Lett.* **1979**, *20*, 3205. (b) Fleming, I.; Iqbal, J. *Tetrahedron Lett.* **1983**, *24*, 2913.

[3] Paterson, I.; Price, L. G. *Tetrahedron Lett.* **1981**, *22*, 2833.

[4] Oida, T.; Tanimoto, S.; Ikehira, H.; Okano, M. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 645.

[5] (a) Bellassoued, M.; Gaudemar, M. *J. Organomet. Chem.* **1984**, *263*, C21. (b) Bellassoued, M.; Ennigrou, R.; Gaudemar, M. *J. Organomet. Chem.* **1988**, *338*, 149.

[6] Fleming, I.; Iqbal, J.; Krebs, E.-P. *Tetrahedron* **1983**, *39*, 841.

[7] Lam, C. N.; Mellor, J. M.; Rawlins, M. F.; Stibbard, J. H. A. *Tetrahedron Lett.* **1978**, *19*, 4103.

[8] Hermann, J. L.; Kieczykowski, G. R.; Schlessinger, R. H. *Tetrahedron Lett.* **1973**, *14*, 2433.

[9] Katzenellenbogen, J. A.; Drumrine, A. L. *J. Am. Chem.* Soc. **1974**, *96*, 5662.

0022-3263/88/1953-3532$01.50/0