Anal. Calcd for $C_{17}H_{19}S_2N$: C, 67.73; H, 6.35. Found: C, 67.48; H, 6.10.

***N*-[4,4-Bis(phenylthio)-3-pentylidene]benzenesulfenamide (14):** 80% yield; oil; NMR ($CDCl_3$) δ 1.6 (s, 3 H, Me), 1.2–1.5 (t, 3 H, Me, J = 7, 5 Hz), 2.7–3.1 (q, 2 H, CH_2, J = 7, 5 Hz), 7.1–7.5 (m, 15 H, arom); IR (film) 1580 cm^{-1} (C=N).

Anal. Calcd for $C_{23}H_{23}NS_3$: C, 67.94; H, 5.70. Found: C, 67.96; H, 5.52.

Acknowledgment. This investigation was supported by Public Health Service Grant No. Ca 14341 from the National Cancer Institute, Department of Health, Education, and Welfare.

Registry No. 1a, 38206-14-3; **1b**, 73557-35-4; **3a**, 65276-67-7; **3b**, 65276-68-8; **3c**, 73557-36-5; **4a**, 73557-37-6; **4b**, 73557-38-7; **4c**, 73557-39-8; **5**, 69753-44-2; **6**, 73557-40-1; **7**, 73557-41-2; **8**, 73557-42-3; **12**, 65276-63-3; (*E*)-**13**, 73557-43-4; (*Z*)-**13**, 73557-44-5; **14**, 73557-45-6; PhSSPh, 882-33-7; $(p\text{-ClPhS})_2$, 1142-19-4; PhSCl, 931-59-9; $PhSO_2SPh$, 1212-08-4.

Generation of α-Oxo Dithioesters by Dithiolanium Ylide Cycloreversion. Synthesis of 2-Acyl-3,6-dihydro-2*H*-thiopyrans

E. Vedejs,* M. J. Arnost, J. M. Dolphin, and J. Eustache

Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706

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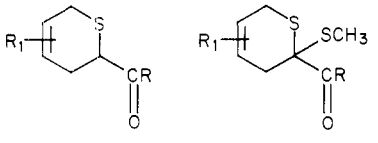
Methylation of 2-acyl-1,3-dithiolanes with CH_3OSO_2F affords sulfonium salts which undergo cycloreversion to α-oxo dithioesters $RCOCS_2CH_3$ (R = CH_3, C_5H_5). In the presence of dienes (2,3-dimethyl-, 1-methyl-, or 1,3-dimethylbutadiene), good yields of 2-acyl-2-(methylthio)-3,6-dihydrothiopyrans are formed. Treatment of the adducts with thiophiles affords 2-acyl-3,6-dihydro-2*H*-thiopyrans **1**. Diels–Alder trapping (15%) of a reactive thioaldehyde (NCCHS) by 2-ethoxybutadiene is also described.

Synthetic projects in our laboratory require a variety of six-membered sulfur heterocycles as intermediates. In particular, α-acyl derivatives such as **1** are desired for

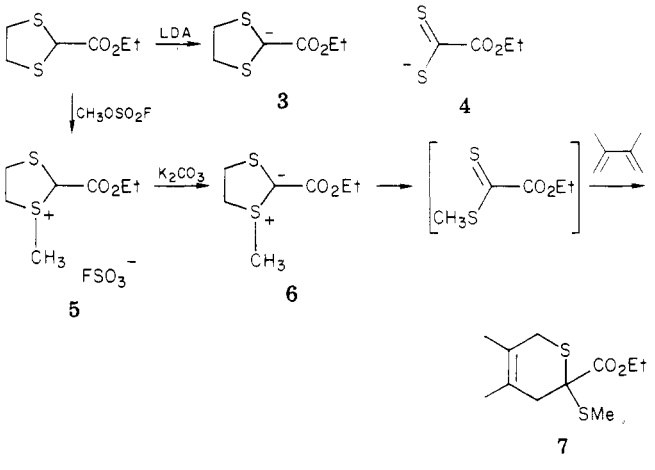


1 **2**

conversion into 2-alkenyl dihydrothiopyrans which are versatile substrates for "ring growing" reactions.[1] The hetero Diels–Alder reaction of dithioesters with dienes is an attractive route to dihydrothiopyrans, and adaptations of this approach are now described.

Cyanodithioformate esters are known to undergo 2 + 4 cycloaddition under mild conditions.[2] This precedent suggests that α-oxo dithioesters would also react readily with Diels–Alder partners to give adducts **2** which might be converted into the desired **1** by desulfenylation. However, α-oxo dithioesters were unknown until recently and only the aromatic derivatives $ArCOCS_2CH_3$ have been reported.[3]

A versatile method for synthesis of dithioesters (XCS_2CH_3) having an electron-withdrawing substitutent (X = RCO, ROCO, etc.) has been developed. The process uses a mildly basic variant of the known cycloreversion of 2-lithiodithiolanes.[4,5] Early experiments under strongly basic conditions suggested that the product dithiocarboxylates (XCS_2^-) would not survive if X is RCO or ROCO. For example, the enolate **3** was generated at −78



5 **6** **7**

°C and was found to be stable to cycloreversion at that temperature. Slow warming to 20 °C and quenching with methyl iodide gave a complex mixture. The expected formation of the known $C_2H_5O_2CCS_2CH_3$[6] could not be confirmed, and whether or not the cycloreversion product **4** was formed could not be established.

More promising results were obtained by using a modified cycloreversion substrate. The starting 2-(carboethoxy)-1,3-dithiolane was first converted into the crystalline sulfonium salt **5** with methyl fluorosulfonate. When **5** was treated with solid K_2CO_3 in the presence of 2,3-dimethylbutadiene (20 °C), the expected thiocarbonyl cycloadduct **7** was obtained in 75% yield. A labile ylide **6** was apparently formed as the intermediate which underwent cycloreversion to $C_2H_5O_2CCS_2CH_3$ under nearly neutral conditions. The same adduct **7** was formed from authentic $C_2H_5O_2CCS_2CH_3$ prepared by the literature method.[6]

(1) Vedejs, E.; Arco, M. J.; Powell, D. W.; Renga, J. M.; Singer, S. P. *J. Org. Chem.* **1978**, *43*, 1185.
(2) Vyas, D. M.; Hay, G. W. *J. Chem. Soc., Perkin Trans. 1* **1975**, 180. Vyas, D. M.; Hay, G. W. *Can. J. Chem.* **1971**, *49*, 3755.
(3) Mayer, R.; Viola, H.; Hopf, B. *Z. Chem.* **1978**, *18*, 90.
(4) Seebach, D. *Synthesis* **1969**, 17. Gonnella, N. C.; Lakshmikanthan, M. V.; Cava, M. P. *Synth. Commun.* **1979**, *9*, 17.
(5) Review of cycloreversion reactions: Bianchi, G.; DeMicheli, C.; Gandolfi, R. *Angew. Chem.* **1979**, *91*, 781.
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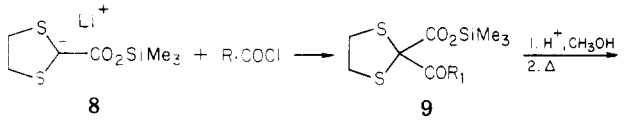
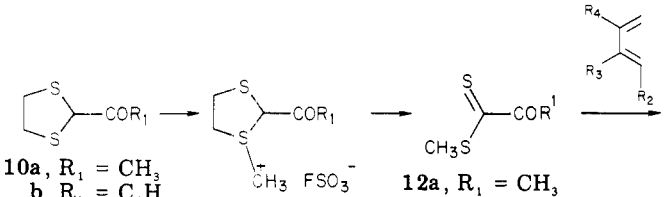
Table I. Generation of XCS_2CH_3 in situ ($X = CH_3CO, C_6H_5CO, C_2H_5OCO$)

dithiolanium salt (% yield of S-methylation)	base/solvent for cycloreversion	diene	adduct (% yield)
5 (93)	K_2CO_3/CH_2Cl_2	2,3-dimethylbutadiene	7 (75)
11a (94)	K_2CO_3/CH_2Cl_2	2,3-dimethylbutadiene	13 (65)
11a	2,6-lutidine/CH_2Cl_2	1-methylbutadiene	14 (79)
11a	2,6-lutidine/CH_2Cl_2	1,3-dimethylbutadiene	15 (82)
11b (86)	K_2CO_3/toluene	2,3-dimethylbutadiene	16 (59)

Similar transformations were achieved with 2-acyl-1,3-dithiolanes **10a** and **10b** as representative examples. A



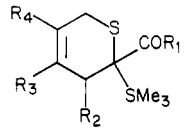
8 9



10a, $R_1 = CH_3$
b, $R_1 = C_6H_5$

11a, $R_1 = CH_3$
b, $R_1 = C_6H_5$

12a, $R_1 = CH_3$
b, $R_1 = C_6H_5$



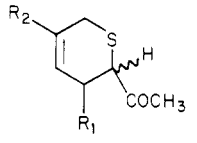
13, $R_2 = H$; $R_1 = R_3 = R_4 = CH_3$
14, $R_1 = R_2 = CH_3$; $R_3 = R_4 = H$
15, $R_1 = R_2 = R_4 = CH_3$; $R_3 = H$
16, $R_1 = C_6H_5$; $R_2 = H$; $R_3 = R_4 = CH_3$

convenient literature procedure is available for the synthesis of **10a** from ethyl acetoacetate,[7] but a more versatile method was required for projects under way in our laboratory. Enolate 8 was acylated with CH_3COCl or PhCOCl to give intermediates **9** which were not isolated. Silyl ester hydrolysis with dilute acid and decarboxylation upon brief heating gave the desired **10a,b**.[8] Alkylation with methyl fluorosulfonate as before afforded sulfonium salts **11a,b**, and treatment with weak base resulted in generation of the reactive α-oxo dithioesters **12a,b**. Either 2,6-lutidine or powdered K_2CO_3 gave comparable yields in the cycloreversion step.

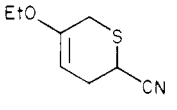
Best results were obtained by in situ generation of **12a** or **12b** in the presence of dienes at room temperature. Under these conditions, the α-oxo dithioesters were trapped in good yield to affort cycloadducts (Table I). Unsymmetrical dienes reacted to give a single major regioisomer in every example studied. Evidence (270-MHz NMR) for a second isomer was observed only in the case of 1,3-dimethylbutadiene, but the minor product (ca. 2%) could not be obtained pure and a choice between the possible alternative structures for the side product (regioisomer vs. diastereomer) could not be made. Previous studies of the Diels–Alder addition of thiocarbonyl compounds have established a similar regiochemical preference, although significant amounts of regioisomers have been observed in some cases.[2,9]

Attempts to isolate the α-oxo dithioesters were successful only in the case of the aromatic derivative **12b**. In the absence of dienes, an intense purple color appeared when the sulfonium salt **11b** was stirred with solid K_2CO_3 in toluene. After chromatography, **12b** was obtained as a purple solid, identical with material prepared by the literature method ($C_6H_5COCH_3 + S_8$; Et_3N; CH_3I).[3] The isolated yield of **12b** was only 30%, compared to overall yields in the 60% range for in situ trapping experiments with dienes. In the case of **11a**, base treatment in the absence of dienes gave only a transient pink color and no evidence for the accumulation of **12a** was observed.

To demonstrate the utility of the Diels–Alder adducts as precursors of 2-acyl-3,6-dihydro-2*H*-thiopyrans (**1**), removal of the SCH_3 group with a variety of thiophiles was investigated. Good results in the desulfenylation of **15** as a representative substrate were obtained by using $(C_6H_5)_3P/C_2H_5OH/CH_3CO_2H$ or p-$CH_3C_6H_4S^-$/DMF.[10] The structure of the product **17** was assigned by 270-MHz NMR analysis. The triphenylphosphine method was also used to convert **14** into **18** in 82% yield.



17, $R_1 = R_2 = CH_3$
18, $R_1 = CH_3$; $R_2 = H$



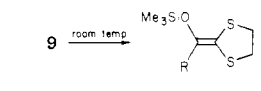
19

In principle, an even more convenient route to analogues of **1** appeared possible by Diels–Alder trapping of a highly reactive thioaldehyde. Although little is known regarding the generation of thioaldehydes, the reported conversion of α-dibromo esters into α-thiono esters by treatment with $K^+{}^-S_2COC_2H_5$ suggested a simple approach.[11] When this procedure was applied to dibromoacetonitrile in the presence of 2-ethoxybutadiene, a modest yield of cycloadduct **19** was isolated. After much experimentation, an optimum yield of 15% was obtained. Although the yield is not competitive with the 2-step procedure involving dithioester cycloaddition followed by desulfenylation, the reaction does demonstrate the generation of the previously unknow thioaldehyde NCCHS.

Summary

Cycloreversion of 1-methyl-1,3-dithiolanium ylides having an electron-withdrawing group in the 2-position is an effective method for generation of dithioesters. The α-oxo dithioesters **12a** and **12b** undergo facile Diels–Alder cycloadditions at room temperature, and nucleophilic desulfenylation of the cycloadducts has been shown to give derivatives of the 2-acyl dihydrothiopyran ring system **1**.

(7) Leir, C. M. *J. Org. Chem.* **1972**, *37*, 887.
(8) If the silyl esters **9** were not treated with acid–methanol before warming to room temperature, significant decarboxylation with simultaneous trimethylsilyl migration occurred.



(9) Ohno, A.; Ohnishi, Y.; Tsuchihashi, G. *Tetrahedron* **1969**, *25*, 871. Friedrich, K.; Zamkanei, M. *Tetrahedron Lett.* **1977**, 2139.
(10) Oki, M.; Fukanoshi, W.; Nakamura, A. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 828, 832.
(11) Beelitz, K.; Hoehne, G.; Praefcke, K. *Z. Naturforsch., B.: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1978**, *33*, 417.
(12) Evidence for the reverse process (dithioester + alkene → dithiolanium ylide) has been reported: Drozd, V. N.; Popova, O. A. *Tetrahedron Lett.* **1979**, 4491.

The synthetic potential of ylide cycloreversion no doubt extends beyond the synthesis of reactive dithioesters. Preparation of a variety of heteroatom derivatives at the oxidation level of carboxylic acids can be imagined, starting from aldehydes, and the process may also be of some interest for olefin generation. We are aware of no previous example of an analogous cycloreversion involving an ylide substrate,[12] although anionic cycloreversions are well-known.[5]

Experimental Section

NMR spectra were obtained at 100 MHz unless stated otherwise (JEOL MH-100). Melting points were obtained by using a hot-stage microscope apparatus and are uncorrected. Preparative thin-layer chromatography (PLC) was performed on Brinkman PF-254 silica gel, 1–1.5-mm layer.

2-[((Trimethylsilyl)oxy)carbonyl]-1,3-dithiolane. A suspension of 1,3-dithiolane-2-carboxylic acid (33.0 g, 0.22 mol) in hexamethyldisilazane (100 mL) was stirred at 20 °C for 5 min and then at 80 °C for 20 min to give a clear solution. Excess hexamethyldisilazane and other volatile components were removed under reduced pressure (10 mm), first at 20 °C and then at 80 °C, with exclusion of moisture. The residue was then distilled to give 2-(carbo(trimethylsiloxy))-1,3-dithiolane as a colorless oil, 46.3 g (94%): bp 71–72 °C (0.05 mm); IR ($CHCl_3$) 1730, 1300 cm^{-1}; NMR ($CDCl_3$) δ 4.72 (1 H, s), 3.50–3.10 (4 H, m), 0.22 (9 H, s); exact mass, m/e 222.0201 (calcd for $C_7H_{14}O_2S_2Si$ 222.0204).

2-Acetyl-1,3-dithiolane (10a). To a solution of mesityl bromide 0.995 g (5 mmol) in THF (10 mL) at −78 °C was added 8.33 mL of a 1.2 M solution of *tert*-butyllithium in pentane under nitrogen. The mixture was stirred for 30 min at −78 °C to give a white suspension.

To this mixture was added (1.11 g, 5 mmol) of 2-(carbo(trimethylsiloxy))-1,3-dithiolane at −78 °C, and the reaction mixture was stirred for 20 min to give a clear yellow solution. This was transferred via cannula into a solution of acetyl chloride (0.36 mL, 5 mmol) in THF (2 mL) cooled to −78 °C. The reaction mixture was stirred for 20 min, and formic acid (0.1 mL) and methanol (0.3 mL) were added while stirring. After 10 min, the bath was removed and the reaction mixture was allowed to warm to room temperature and then stirred for 30 min. Most of the solvents were evaporated under reduced pressure and the residue was chromatographed (preparative layer chromatography, silica gel Merck 60 PF-254) to give 2-acetyl-1,3-dithiolane **10a**: 507 mg (68%); R_f 0.35 (30% ether in hexane); NMR and IR spectra identical with those reported in the literature.[7]

2-Benzoyl-1,3-dithiolane (10b). The same procedure as described for **10a** was used on a 5-mmol scale. After concentration of solvents after the solution was warmed to room temperature, the product was purified by filtration chromatography over silica gel (1.5 × 15 cm) with 30% ether–hexane. The eluate was concentrated to give a partially crystalline solid. Recrystallization from ether–hexane (0 °C) gave **10b**: 0.7 g (67%); mp 101–102 °C; IR ($CDCl_3$) 1680 cm^{-1}; NMR ($CDCl_3$) δ 7.9–8.2 (2 H, m), 7.4–7.7 (3 H, m), 5.78 (1 H, s), 3.36 (4 H, s); exact mass, m/e 210.018 (calcd for $C_{10}H_{10}OS_2$ 210.0173).

1-Methyl-2-(carboethoxy)-1,3-dithiolanium Fluorosulfonate (5). To a stirred solution of 2-(carboethoxy)-1,3-dithiolane (3.56 g, 20 mmol) in dry CH_2Cl_2 (30 mL, distilled from P_2O_5) was added methyl fluorosulfonate (1.8 mL, 2.2 mmol) at room temperature. After ca. 1 h, the salt began to crystallize. After 16 h, the precipitate was collected, washed with ether, and dried under vacuum (50 °C, 0.1 mm, 2 h) to give 5.43 g (93%) of a white solid (**5**): mp 148–150 °C; IR (KBr) 1720 cm^{-1}; NMR (CD_3SOCD_3) δ 6.02 (1 H, s), 3–4.6 (6 H, m), 2.84 (3 H, s), 1.27 (3 H, t, J = 7 Hz). This material was somewhat hygroscopic and was used without further purification.

1-Methyl-2-acetyl-1,3-dithiolanium Fluorosulfonate (11a). 2-Acetyl-1,3-dithiolane (15.4 g, 104 mmol) was dissolved in methylene chloride (100 mL, distilled from P_2O_5) and cooled to −20 °C. Methyl fluorosulfonate (Aldrich, 9.4 mL, 116 mmol, freshly distilled) was added via syringe. After 1 h at −20 °C, the reaction was warmed to room temperature. After 4 h, a precipitate formed. The reaction was stirred for an additional 9 h and was then filtered. The filtrate was washed with methylene chloride (50 mL) and ether (100 mL) and dried under vacuum to furnish 25.7 g (94.3%) of the salt as a slightly pink powder: mp 100–105 °C; NMR (CD_3CN) δ 2.4 (3 H, s), 3–4.2 (4 H, m), 6.1 (1 H, s). This material was used without further purification.

1-Methyl-2-benzoyl-1,3-dithiolanium Fluorosulfonate (11b). A solution of 2-benzoyl-1,3-dithiolane (0.84 g, 4 mmol) in dry CH_2Cl_2 (10 mL) was treated with methyl fluorosulfonate (0.51 g, 4.5 mmol) as described for **11a**. The precipitated salt–CH_2Cl_2 mixture was diluted with ether (10 mL), filtered, and washed with ether to give **11b** as a white solid: mp 116–120 °C; NMR (CD_3CN) δ 7.8–8.04 (2 H, m), 7.5–7.7 (3 H, m), 6.78 (1 H, s), 3.0–4.3 (4 H, m), 2.88 (3 H, s). This material was used without further purification.

Diels–Alder Trapping. In Situ Generation of Dithioesters. Ethyl 3,6-Dihydro-4,5-dimethyl-2-(methylthio)-2*H*-thiopyran-2-carboxylate (7). A suspension of 1-methyl-2-(carboethoxy)-1,3-dithiolanium fluorosulfonate **5** (0.087 g, 0.3 mmol), finely powdered K_2CO_3 (0.1 g, 0.7 mmol), and 2,3-dimethylbutadiene (0.25 g, 3 mmol) in dry CH_2Cl_2 (3 mL, distilled from P_2O_5) was stirred for 16 h at room temperature. A faint purple color was visible during the first few hours. After filtration through Celite and solvent removal (aspirator), the residue was separated (PLC, silica gel, 30% ether–hexane) to give **7** as a major UV-active band: R_f 0.5; 0.055 g (75%); colorless oil; IR (neat) 1740 cm^{-1}; NMR ($CDCl_3$) δ 4.26 (2 H, q, J = 7 Hz), 3.32 (1 H, br d, J = 16 Hz), 2.92 (2 H, overlapping doublets, J = 16, 17 Hz), 2.46 (2 H, d, J = 17 Hz), 2.1 (3 H, s), 1.71 (6 H, br s), 1.32 (3 H, t, J = 7 Hz); exact mass, m/e 246.0749 (calcd for $C_{11}H_{18}O_2S_2$ 246.0748).

The same product was formed when *S*-methyl *O*-ethyl dithiooxalate[6] was treated with excess 2,3-dimethylbutadiene at room temperature.

2-Acetyl-3,6-dihydro-4,5-dimethyl-2-(methylthio)-2*H*-thiopyran (13). To a suspension of 1-methyl-2-acetyl-1,3-dithiolanium fluorosulfonate (262 mg, 1 mmol) in CH_2Cl_2 (5 mL) containing 2,3-dimethylbutadiene (0.7 g, 8.5 mmol) was added finely powdered potassium carbonate (0.4 g, 2.9 mmol). The slightly purple mixture was stirred for 16 h and filtered, the filtrate was evaporated, and the residue was chromatographed (PLC, silica gel, 2 elutions) with 10% ether/hexane. The major UV-active band (R_f 0.5) gave the desired **13** (0.14 g, 65%), which crystallized on standing and could be recrystallized from ether–hexane: mp 70.5–71 °C; IR ($CDCl_3$) 1690 cm^{-1}; NMR ($CDCl_3$) δ 3.18 (1 H, br d, J = 17 Hz), 2.82 (1 H, br d, J = 17 Hz), 2.76 (1 H, br d, J = 17 Hz), 2.39 (1 H, br d, J = 17 Hz), 2.32 (3 H, s), 1.92 (3 H, s), 1.68 (6 H, br s); exact mass, m/e 216.0642 (calcd for $C_{10}H_{16}OS_2$ 216.0642).

2-Benzoyl-3,6-dihydro-4,5-dimethyl-2-(methylthio)-2*H*-thiopyran (16). To a suspension of 1-methyl-2-benzoyl-1,3-dithiolanium fluorosulfonate (0.324 g, 1 mmol) in toluene (15 mL) containing 2,3-dimethylbutadiene (1.5 mL, ca. 25 mmol) was added finely powdered potassium carbonate (0.3 g, 2.2 mmol). The mixture was stirred for 60 h under N_2 at 20 °C and then filtered (Celite), the filtrate was evaporated, and the residue was chromatographed (PLC, 2 elutions) with 20% ether/hexane as eluant. The major UV-active band (R_f 0.4) afforded the desired **16** (0.164 g, 59%) which crystallized on standing and was recrystallized from ether: mp 79–80 °C; IR ($CDCl_3$) 1660, 1590, 1570 cm^{-1}; NMR ($CDCl_3$) δ 8.0 (2 H, m), 7.1–7.4 (3 H, m), 3.20 (1 H, br d, J = 16 Hz), 2.76 (2 H, 2 br d overlapping), 2.50 (1 H, d, J = 17 Hz), 1.96 (3 H, s), 1.64 and 1.56 (6 H, 2 br s overlapping); exact mass, m/e 278.0794 (calcd for $C_{15}H_{18}OS_2$ 278.0799).

2-Acetyl-3,6-dihydro-3,5-dimethyl-2-(methylthio)-2*H*-thiopyran (15). A suspension of 1-methyl-2-acetyl-1,3-dithiolanium fluorosulfonate (9.91 g, 37.8 mmol) in CH_2Cl_2 (120 mL, freshly distilled from P_2O_5) was stirred with a 3:1 mixture of 1,3-dimethylbutadiene and 1,1-dimethylbutadiene (148 g, ca. 135 mmol of 1,3 isomer).[13] After addition of 2,6-lutidine (8.0 mL, 69 mmol, distilled from BaO and stored over KOH), the reaction mixture was stirred at room temperature for 60 h, at which time it was homogeneous. The mixture was poured into 10% HCl (100 mL) and ether (150 mL) was added. The layers were separated and the organic layer was washed with 10% HCl (2 × 50 mL) and brine and then dried ($MgSO_4$). The solvent was removed (as-

(13) Bartlett, P. D.; Wallbildich, G.; Montgomery, L. *J. Org. Chem.* **1967**, *32*, 1290.

pirator), giving 10.1 g of a yellow oil which was filtered through 20 g of silica gel with 3% ethyl acetate/hexane. After solvent evaporation, a yellow solid was obtained which was stirred with methanol (50 mL) and filtered to give white crystals. Sublimation (60–70 °C (0.08 mm)) gave 5.20 g, mp 76–78 °C. Concentration of the methanol to 15 mL and cooling gave an additional 1.48 g of product (total yield 82%). No evidence for adduct formation from the contaminating 1,1-dimethylbutadiene was found. The crystalline product was identified as **15**: IR ($CBrCl_3$) 1710 cm^{-1}; NMR ($CDCl_3$) δ 5.43 (1 H, br d, J = 6 Hz), 3.2 (1 H, d, J = 17 Hz), 2.68 (1 H, d, J = 17 Hz), 2.61 (1 H, qd, J = 7, 6 Hz), 2.36 (3 H, s), 1.97 (3 H, s), 1.75 (3 H, br s), 1.09 (3 H, d, J = 7 Hz); exact mass, m/e 216.0642 (calcd for $C_{10}H_{16}OS_2$ 216.0643).

2-Acetyl-3,6-dihydro-3-methyl-2-(methylthio)-2*H*-thiopyran (14). The same procedure was used as described for the preparation of **15** (20-mmol scale). Sublimation (50–60 °C (0.08 mm)) gave **14** as white crystals: mp 61–63 °C (79%); IR ($CBrCl_3$) 1705 cm^{-1}; NMR ($CDCl_3$) δ 5.75 (2 H, m), 3.29 (1 H, br d, J = 17 Hz), 2.88 (1 H, dd, J = 17, 4 Hz), 2.63 (1 H, m), 2.37 (3 H, s), 1.99 (3 H, s), 1.13 (3 H, d, J = 7 Hz); exact mass, m/e 202.0496 (calcd for $C_9H_{14}OS_2$ 202.0486).

2-Acetyl-3,6-dihydro-3,5-dimethyl-2*H*-thiopyran (17). Triphenylphosphine Method.[10] A solution of 2-acetyl-3,6-dihydro-3,5-dimethyl-2-(methylthio)-2*H*-thiopyran (22.2 g, 103 mmol), **15**, in absolute ethanol (250 mL) was stirred with triphenylphosphine (84.0 g, 321 mmol) and acetic acid (7.4 mL, 130 mmol). The reaction flask was vented through a bubbler containing bleach solution to absorb methanethiol, and the mixture was refluxed for 5 days. After the solution was cooled to room temperature, methyl iodide (20 mL, 320 mmol) was added to consume the remaining triphenylphosphine. Water (100 mL) was added and the mixture was extracted with hexane (5 × 100 mL). The hexane layer was dried (Na_2SO_4) and the solvent was removed (rotary evaporator). Bulb-to-bulb distillation (at 0.05 mm, 50–60 °C) afforded the product **17** (14.8 g, 85%) as a colorless oil, mixture of diastereomers: IR (neat) 1715 cm^{-1}; 270-MHz NMR ($CDCl_3$) of major diastereomer δ 5.43 (1 H, m), 3.19 (1 H, d, J = 4 Hz), 2.89 (1 H, J = 17 Hz), 2.75 (1 H, d, J = 17 Hz), 2.63 (1 H, m), 2.33 (3 H, s), 1.72 (3 H, br s), 1.10 (3 H, d, J = 7 Hz); 270-MHz NMR of minor diastereomer δ 5.43 (1 H, m), 3.69 (1 H, d, J = 4.4 Hz), 3.02 (1 H, d, J = 17 Hz), 2.87 (1 H, d, J = 17 Hz), 2.63 (1 H, m), 2.25 (3 H, s), 1.74 (3 H, br s), 1.03 (3 H, d, J = 7 Hz); exact mass, m/e 170.0768 (calcd for $C_9H_{14}OS$ 170.0766).

Preparation of 17 Using Sodium *p*-Toluenethiolate.[10] A solution of *p*-toluenethiol (0.062 g) was stirred with sodium hydride (0.004 g, hexane washed) and DMF (1 mL, distilled from CaH_2) until H_2 evolution ceased. A solution of **15** (0.065 g) in minimal DMF was added and the mixture was stirred for 4 h at 20 °C. The product was partitioned between water–hexane, and the hexane layer was dried ($MgSO_4$) and evaporated to give an oily residue. Separation by PLC (silica gel, 30% ether–hexane) gave three zones: R_f 0.8, *p*-$CH_3C_6H_4SSCH_3$, R_f 0.5, recovered **15** (0.004 g), and R_f 0.4, **17** (0.040 g, 78%). The product **17** was identical with material prepared by the triphenylphosphine method.

2-Acetyl-3,6-dihydro-3-methyl-2*H*-thiopyran (18). The same triphenylphosphine procedure was used as described for **17** (82% yield). The product was obtained as a mixture of diastereomers: colorless oil; IR (neat) 1715 cm^{-1}; NMR ($CDCl_3$) of major diastereomer δ 5.77 (2 H, unresolved br s), 3.26 (1 H, d, J = 4 Hz), 2.3–3.2 (3 H, unresolved), 2.35 (3 H, s), 1.14 (3 H, d, J = 7 Hz); NMR ($CDCl_3$) of minor diastereomer δ 5.77 (2 H, unresolved br s), 3.75 (1 H, d, J = 5 Hz), 2.3–3.2 (3 H, unresolved), 2.28 (3 H, s), 1.05 (3 H, d, J = 7 Hz); exact mass, m/e 156.0608 (calcd for $C_8H_{12}OS$ 156.06088).

4-Ethoxy-3,6-dihydro-2*H*-thiopyran-2-carbonitrile (19). A solution of 2-ethoxybutadiene (4 g, 40 mmol) in DMF (20 mL, distilled from CaH_2) was heated to 50 °C. Dibromoacetonitrile (0.5 g, 2.5 mmol) was added. A solution of 0.8 g of $K^+{}^-S_2COC_2H_5$ in DMF (20 mL) was then added dropwise over 10 min. The mixture was stirred at 50 °C for 15 min and was then cooled to 20 °C. Partition between water (50 mL) and pentane (100 mL) gave an organic layer which was dried ($MgSO_4$). Removal of pentane by distillation through a Vigreux column gave a residue which was distilled under aspirator vacuum to recover ethoxybutadiene. The yellow residual oil was purified by high-performance LC (Waters Porasil A, 4 ft × $^3/_8$ in., 3% ethyl acetate/hexane, 8 mL/min). The product **19** was obtained as a white solid (0.06 g, 15%), recrystallized from pentane: mp 53–55 °C; IR (CCl_4) 2230, 1670 cm^{-1}; NMR ($CDCl_3$) δ 4.68 (1 H, br s), 3.72 (2 H, m), 3.58 (2 H, AB q, J = 17.5 Hz), 2.7 (2 H, br s), 1.29 (3 H, t, J = 7 Hz); exact mass, m/e 169.0564 (calcd for $C_8H_{11}NOS$ 169.05305).

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Registry No. **5**, 73496-44-3; **6**, 73496-45-4; **7**, 73496-46-5; **10a**, 33406-25-6; **10b**, 21504-08-5; **11a**, 73496-48-7; **11b**, 73496-50-1; **12a**, 73496-51-2; **12b**, 66739-97-7; **13**, 73496-52-3; **14**, 73496-53-4; **15**, 73496-54-5; **16**, 73496-55-6; *cis*-**17**, 73496-56-7; *trans*-**17**, 73496-57-8; *cis*-**18**, 73496-58-9; *trans*-**18**, 73496-59-0; **19**, 73496-60-3; 1,3-dithiolane-2-carboxylic acid, 5616-65-9; 2-[((trimethylsilyl)oxy)-carbonyl]-1,3-dithiolane, 73496-61-4; 2-(carboethoxy)-1,3-dithiolane, 20461-99-8; methyl fluorosulfonate, 421-20-5; 2,3-dimethylbutadiene, 513-81-5; 2-methyl-1,3-pentadiene, 1118-58-7; 1,3-pentadiene, 504-60-9; 2-ethoxybutadiene, 4747-05-1; $K^+{}^-S_2COC_2H_5$, 140-89-6; dibromoacetonitrile, 3252-43-5.

Reactions of 2,3-Diphenylthiirene 1,1-Dioxide with Nucleophiles

Bruce B. Jarvis* and G. Patrick Stahly

Department of Chemistry, University of Maryland, College Park, Maryland 20742

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A series of nucleophiles was allowed to react with 2,3-diphenylthiirene 1,1-dioxide (**1**) in dipolar aprotic solvents to produce a variety of derivatives. Fluoride ion gave diphenylacetylene and (*E*)-1,2-diphenylvinylsulfonyl fluoride (**2**); thiophenoxide gave (*E*)-1,2-diphenyl-2-(thiophenoxyl)vinylsulfinate which gave the corresponding methyl sulfone **5** on treatment with methyl iodide. Azide ion gave a variety of products including diphenylvinyl azides **12** and **13**, 2,3-diphenylazirine (**14**), 2,6-diphenyl-4-[(*E*)-diphenylvinyl]-1,3,4,5-thiatriazine 1,1-dioxide (**15**), benzil (**16**), 4,5-diphenyltriazole (**17**), 2,4,5-triphenylimidazole (**18**), and (*Z*)-1,2-diphenyl-2-azidovinylsulfinate which gave the corresponding methyl sulfone **22** on treatment with methyl iodide. The diphenylvinyl group was removed from the new heterocycle **15** by ozonolysis followed by mild base hydrolysis to yield the thiatriazine 1,1-dioxide **20**. Compound **20** undergoes thermolysis at 40 °C to give stilbenes, and **20** also undergoes a facile base-catalyzed extrusion of sulfur dioxide to give imidazole **18**.

The reactions of 2,3-diphenylthiirene 1,1-dioxide (**1**) with nucleophiles have provided a variety of new and interesting compounds.[1] In general, it has been found that strongly basic nucleophiles attack the sulfonyl sulfur atom of **1**

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