$MgSO_4$. Evaporation of solvent and purification gave 1α-hydroxy derivative 8, in 50% yield: mass spectrum, m/e 402 (M^+, 40), 370 (70), 329 (35), 235 (45), 135 (100); NMR δ 0.57 (s, 3 H, 18-CH_3), 0.64 (m, 1 H, 4-H), 0.99 (d, J = 5.9 Hz, 21-CH_3), 3.26 (s, 1 H, 6-OCH_3), 3.66 (s, 3 H, 23-$COOCH_3$), 4.17 (d, J = 8.9 Hz, 1 H, 6-H), 4.22 (m, 1 H, 1β-H), 4.96 (d, J = 8.9 Hz, 1 H, 7-H), 5.16 (s, 1 H, 19(*Z*)-H), 5.24 (s, 1 H, 19(*E*)-H). The 1α-hydroxycyclovitamin 8 was dissolved in 0.5 mL of glacial acetic acid and heated at 55 °C for 15 min. Products (1c and the corresponding 5,6-trans isomer in ca. 3:1 ratio) were extracted with ether, and the ether phase was washed as before. Compound 1c was purified by TLC (50% EtOAc in hexane, R_f 0.32) followed by high-pressure LC (6.4 × 250 mm column, 2.5% 2-propanol in hexane, at 2 mL/min and 900 psi). Product 1c, eluting at 63 mL, was recycled through the column and obtained in pure form in 20.2% yield from 6: UV λ_{max} 264 nm (ε, 18 000); mass spectrum, m/e 430 (M^+, 10), 370 (65), 269 (10), 134 (100); NMR δ 0.58 (s, 3 H, 18-CH_3), 0.99 (d, J = 5.9 Hz, 3 H, 21-CH_3), 2.03 (s, 3 H, 3-$OCOCH_3$), 3.66 (s, 3 H, 23-$COOCH_3$), 4.4 (m, 1 H, 1-H), 5.01 (s, 1 H, 19(*Z*)-H), 5.21 (m, 1 H, 3α-H), 5.34 (s, 1 H, 19(*E*)-H), 6.02 (d, J = 11.0 Hz, 1 H, 7-H), 6.34 (d, J = 11.0 Hz, 1 H, 6-H). Mild hydrolysis of 1c (75 μL of 0.1 M KOH/MeOH and 200 μL of ether, 15 °C, 60 min) provided 1b: UV λ_{max} 264 nm (ε, 18 000); high-resolution mass spectrum, calcd for $C_{24}H_{36}O_4$ 388.2614, found 388.2645; mass spectrum, m/e (relative intensity) 388 (18), 370 (61), 357 (3), 352 (24), 314 (1), 287 (1), 269 (4), 251 (7), 152 (31), 134 (100); NMR δ 0.58 (s, 3 H, 18-CH_3), 0.99 (d, J = 5.9 Hz, 3 H, 21-CH_3), 3.67 (s, 3 H, $COOCH_3$), 4.23 (m, 1 H, 3α-H), 4.43 (m, 1 H, 1β-H), 5.00 (s, 1 H, 19(*Z*)-H), 5.33 (s, 1 H, 19(*E*)-H), 6.02 (d, J = 11.0 Hz, 1 H, 7-H), 6.38 (d, J = 11.0 Hz, 1 H, 6-H). Hydrolysis of 1b in 10% KOH/90% methanol at 60 °C for 30 min followed by neutralization and filtration in 100% ethanol gives quantitative yields (by TLC and UV) of the natural product 1a.

Comparison with Biologically Generated 1b. The low-resolution mass spectrum and the UV spectrum for synthetic 1b were identical with the spectra obtained for the methylated metabolite isolated from 1,25-$(OH)_2D_3$-treated rats.[3] (Direct comparison of NMR spectra was not possible because the low quantities of isolated natural product[3] precluded NMR measurements.) For confirmation of chromatographic identity, [3α-^{3}H]calcitroic acid was obtained from the livers of rats dosed with [3α-^{3}H]-1α,25-dihydroxyD_3 and converted to its methyl ester (1b) as described by Esvelt et al.[3] This material (6500 dpm) was combined with 2 μg of synthetic 1b and the mixture was chromatographed on high-pressure LC using the 4.6 × 250 mm column eluted with 8% 2-propanol in hexane, and the absorbance was monitored at 254 nm. Fractions were collected, evaporated, and counted. Radioactivity coeluted exactly with the UV-absorbing peak due to synthetic 1b (elution volume, 40 mL).

Registry No. 1a, 71204-89-2; 1b, 71203-48-0; 1c, 75716-71-1; 1c 5,6-*trans* isomer, 75716-72-2; 2, 1474-14-2; 3, 33168-65-9; 4a, 75716-73-3; 4b, 75716-74-4; 5, 75716-75-5; 6, 75716-76-6; 6 3-tosyl derivative, 75731-72-5; 7, 75716-77-7; 8, 75731-73-6.

(1) (a) Savino, P. D.; Bereman, R. D. *Inorg. Chem.* **1973**, *19*, 173-6. (b) Bereman, R. D.; Good, M. L.; Kalbacher, B. J.; Buttone, J. *Ibid.* **1976**, *15*, 618-21. (c) Bereman, R. D.; Nalewajek, D. *Ibid.* **1970**, *16*, 2687-91; (d) *Ibid.* **1978**, *17*, 1085-7.

1,3-Dithiane-2-carbodithioate: Synthesis and Reactivity Patterns

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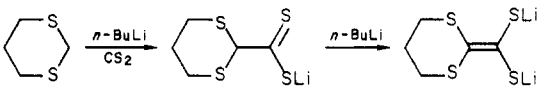
Introduction

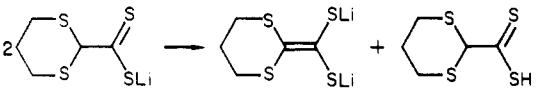
Work in these laboratories had centered on the design and syntheses of novel sulfur-containing molecules which promise to generate unique coordination chemistry with transition metals.[1] For the most part, this work has concentrated on new dithiolate and dithiocarbamate ligands. Our recent attempts to investigate the coordination chemistry of molecules containing the "tetrathiaethylene" unit have resulted in the syntheses of several new and interesting organosulfur species. In this note we report the syntheses and alkylation products of the 1,3-dithiane-2-carbodithioate dianion (2) and the corresponding monoanion (1).

Scheme I



1 2

Scheme II

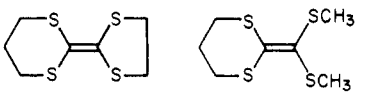


2 3

The chemistry of the 1,3-dithiane ring system is quite extensive. 1,3-Dithiane is probably best known as an acyl anion equivalent.[2] However, derivatives of 1,3-dithiane have also been of considerable interest in studies concerned with the conformational properties of heterocyclic molecules.[3] Ketene thioacetals have received considerable attention lately as useful organic intermediates.[4] The compounds reported here should be of interest in all of these areas. The most promising aspect of this work may be the ability to produce "asymmetric" molecules containing the tetrathiaethylene unit. Enormous interest in molecules containing this unit has been generated by the ability of this class of compounds to form charge-transfer complexes with TCNQ and some of its derivatives.[5] Until now, however, there has not been a facile method to prepare unsymmetrical tetrathiaethylene derivatives.

Discussion

Dilithio-1,3-dithiane-2-carbodithioate can be prepared from lithio-1,3-dithiane and CS_2 followed immediately by a second equivalent of *n*-BuLi as outlined in Scheme I. The second equivalent of *n*-BuLi must be added quickly since the C-2 proton of the monoanion 1 is extremely acidic due to its position α to two sulfides[6] as well as α to the dithiocarboxylate group. Failure to add *n*-BuLi results in a disproportionation reaction (Scheme II) to yield 2 and the extremely unstable dithioacid 3 which quickly decomposes. Dianion 2 is a white powder which can be alkylated without further isolation or it can be isolated and stored under argon at a temperature lower than −20 °C. Temperatures higher than −20 °C or contact with air instantly transform 2 into a smelly red oil of unknown composition. 2 can be alkylated with normal alkyl halides. For example, reaction of 2 with 1,2-dibromoethane yields 2-(1,3-dithiolan-2-ylidene)-1,3-dithiane (4) while reaction with 2 equiv of methyl iodide produces the dimethyl dithioacetal 5.



4 5

(2) Corey, E. J.; Seebach, D. *J. Org. Chem.* **1975**, *40*, 231-7.
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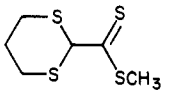
Alkylation of the monoanion 1 can be achieved if the reaction with alkylating agent is rapid enough to avoid disproportionation of 2. For example, addition of CS_2 to lithio-1,3-dithiane followed immediately by CH_3I produces the methyl ester of 1,3-dithiane-2-dithiocarboxylic acid (6).



6

All compounds were identified by NMR and elemental analyses.

Experimental Section

All reactions were carried out with standard Schlenk techniques employing anhydrous Ar. THF was freshly distilled from Na/benzophenone just prior to use. Dithiane was either prepared by the standard procedure[7] or obtained from Aldrich Chemical Co. and was sublimed prior to use. *n*-BuLi was used as a 1.6 M solution in hexane.

NMR spectra were obtained in $CDCl_3$, employing a Varian HA-100 spectrometer. Elemental analyses were obtained from Atlantic Microlabs, Atlanta, GA.

Dilithio-1,3-dithiane-2-carbodithioate (2). *n*-BuLi (10.4 mL, 1.6 M in hexane) was added to a solution of 2 g of dithiane in 100 mL of THF at −28 °C over a 5-min period. This solution was stirred for 1.5 h after which CS_2 (0.95 mL) was added to yield a red solution. Immediately an additional 10.4 mL of *n*-BuLi solution was added all at once. In 5–10 min, a white solid (2) precipitated. This solid was isolated by filtration in a standard Schlenk filter which was jacketed with dry ice. The solid was dried under vacuum while maintaining the low temperature. Once dry, 2 was stored under Ar in a freezer. The yield was essentially quantitative.

Alkylation of 2. 2-(1,3-Dithiolan-2-ylidene)-1,3-dithiane (4). 2 was prepared as above and kept as a slurry in THF at −28 °C. To this was added 1 equiv of anhydrous ethylene bromide. The reaction mixture immediately became a homogeneous solution. After the mixture was stirred for 1 h, the dry ice bath was removed, and the solvent was removed by vacuum. Ethanol (50 mL) was added to give a light yellow solid. (From this point anhydrous conditions were no longer necessary.) The solid was recrystallized from ethanol and chloroform to yield yellow crystals: yield 45–50%; mp 104–105 °C; NMR ($CDCl_3$) δ 2.17 (2 H, m), 2.82 (4 H, singlet), 3.4 (4 H, m). Anal. Calcd for $C_7H_{10}S_4$: C, 37.80; H, 4.53; S, 57.66. Found: C, 37.85; H, 4.52; S, 57.59.

2-[Bis(methylthio)methylene]-1,3-dithiane (5). 2 was prepared as above and kept as a slurry at −28 °C. To this was added 2 equiv of methyl iodide. The reaction mixture became a homogeneous solution. After the mixture was stirred for 1 h, the dry ice both was removed and solvent was removed by vacuum. Ethanol (50 mL) was added to give a yellow solid. Crystallization from ethanol/chloroform gave 5: yield ~50%; mp 110–112 °C; NMR ($CDCl_3$) δ 2.0 (2 H, m), 2.35 (6 H, s), 2.98 (4 H, m).

Alkylation of 1. Methyl 1,3-Dithiane-2-dithiocarboxylate (6). Dithiane was treated with 1 equiv of *n*-BuLi at −28 °C. After 1.5 h, CS_2 was added all at once followed immediately by 1 equiv of CH_3I. The red solution turned yellow upon addition of the CH_3I. The solution was warmed and solvent was removed by vacuum. Addition of ethanol produced a yellow solid which was recrystallized from ethanol and chloroform: yield 85%; mp 125–126 °C; NMR ($CDCl_3$) δ 2.0 (2 H, m), 2.27 (3 H, s), 2.53 (2 H, m), 5.27 (1 H, s). Anal. Calcd for $C_7H_{12}S_4$: C, 34.25; H, 4.80; S, 60.96. Found: C, 34.22; H, 4.82; S, 60.89.

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Registry No. 2, 75812-75-8; 4, 75812-76-9; 5, 75812-77-0; 6, 75812-78-1; dithiane, 505-23-7; CS_2, 75-15-0; ethylene bromide, 106-93-4.

(7) Corey, E. J.; Seebach, D. *J. Org. Chem.* **1970**, *35*, 72–4.

Cyclic Phosphonium Ylides. A Short Synthesis of Gossyplure[1]

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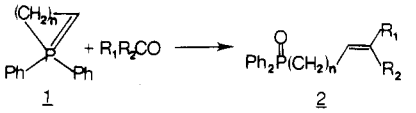
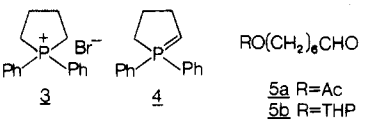
The use of triarylphosphonium ylides in organic chemistry, particularly in the Wittig olefination reaction, has become a cornerstone of synthetic methodology. In contrast to the extensive knowledge in this area, the corresponding cyclic phosphonium ylides have been investigated only sporadically and have never been exploited in a synthetic manner.[2] In principle, such ylides of the general structure 1 possess considerable synthetic potential because, for example, a Wittig reaction therewith generates an olefinic phosphine oxide 2, upon which subsequent chemical transformations can be effected. This note re-



1 2

ports the first synthetic utilization of a cyclic phosphonium ylide by describing the incorporation of the five-membered ylide 4 into a short synthesis of the sex pheromone of the female pink bollworm moth gossyplure, the 1:1 mixture of (7*Z*,11*Z*)- and (7*Z*,11*E*)-7,11-hexadecadien-1-yl acetates **9b** and **10b**.[3]

The introduction of the 7*Z* olefin was accomplished in a straightforward manner via a Wittig reaction. The salt 1,1-diphenylphospholanium bromide (3), prepared in



3 4 5a R=Ac 5b R=THP

quantity by variation of a recent procedure,[4] was converted to ylide 4 upon treatment with potassium *tert*-butoxide in THF at room temperature. Addition of either 7-acetoxyheptanal (**5a**)[5] or 7-(2-tetrahydropyranyloxy)heptanal (**5b**)[6] to the ylide gave the corresponding diphenylphosphine oxide *Z* olefin **6** or **6b** in high yield. The *Z*

(1) Contribution no. 555 from the Syntex Research Institute of Organic Chemistry.

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