Mono- and Bis-carbonyl Methylenation of Thiolane-2,5-diones (Succinic Thioanhydrides)[1]

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While direct carbonyl olefination of *cyclic* anhydrides[2] and thioanhydrides[3] has previously been observed, such reactions have been successful *only* in cases utilizing stabilized phosphorus ylides. Methylenation of lactones,[4] esters,[4,5] and thioesters[6] has been accomplished by use of titanium-mediated methylene transfer agents such as Tebbe's reagent, Grubbs' titanocyclobutanes, and more recently, by Petasis and Bzowej using dimethyltitanocene. In contrast, methylenation of anhydrides[7a] with titanocyclobutanes occurs with rearrangement to afford titanium enolates.

Our interest in the latter titanium-based reagents stemmed from other work in our laboratory on the synthesis of oxygen and sulfur heterocycles with exocyclic carbon–carbon double bonds α to heteroatoms. This work has prompted us to investigate methods for the synthesis of enol thiolactones and dienol thioethers by direct carbonyl methylenation of cyclic thioanhydrides. Preliminary work on reaction of the Tebbe reagent[4c] with thioanhydride **1d** indicated that sequential methylenation of carbonyl groups was occurring; however, the reaction was not useful, due to low yields and isomerization of the presumed dimethylene intermediate **4d** to the corresponding thiophene **5d**.

In view of the suspected Lewis acid behavior of the Tebbe reagent,[7b] it thus appeared that an aluminum-free reagent such as dimethyltitanocene would be more suitable for methylenation of five-membered ring thioanhydrides. Thermolysis of dimethyltitanocene[5c] in the presence of cyclic thioanhydrides **1a-1f** (Scheme 1) does result in the desired mono- and dimethylenated products **2a-2f**, **3b**, **3c**, and **4a–4f**, respectively (Table 1), in good yields. The first methylenation is observed to be faster than the second; thus, by using dimethyltitanocene as the limiting reagent, the monomethylenated products can be isolated preparatively. Furthermore, no isomerization of the dienol thioethers **4a-4f** to the corresponding thiophenes **5a-5f** was observed under these reaction conditions.

Scheme 1

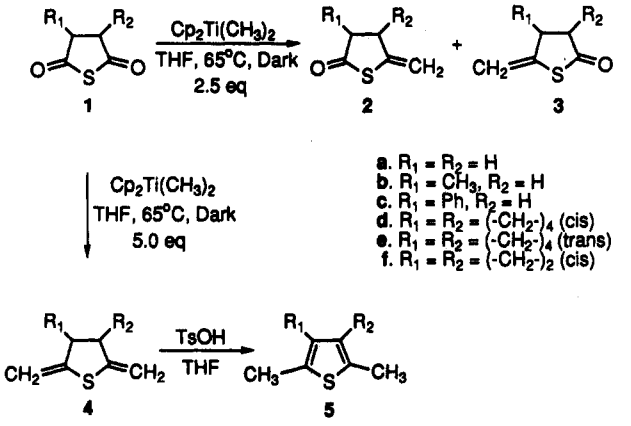
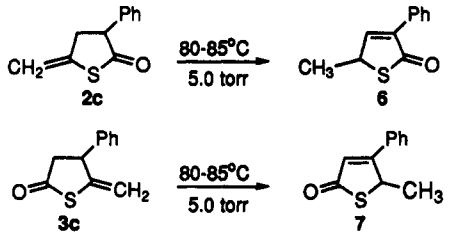


Table 1. Thioanhydride Olefination

product[a] 2, 3	yields[b] (%)	product[a] 4	yields[b] (%)
2a	59	**4a**	40[c,d]
2b (74%), **3b** (26%)[e]	55	**4b**	75[d]
2c (65%), **3c** (35%)[e]	65	**4c**[f]	78[d]
2d	79	**4d**	84
2e	66	**4e**	81
2f	53	**4f**	74

[a] Progress of all reactions was monitored by gas chromatography. [b] Isolated yields after chromatography. [c] Isolated yield was low due to volatility. [d] Yields determined from isolated dimethylthiophenes. [e] Ratio of isomers was determined by quantitative ^1H and ^{13}C NMR and by gas chromatography. [f] Diene **4c** was not isolated.

Scheme 2



A typical procedure for monomethylenation involves reaction of 15.0 mmol of dimethyltitanocene with 6.0 mmol of cyclic thioanhydride in THF at 65 °C for 22–26 h under argon, with exclusion of light. Under such conditions the enol thiolactones **2a-2f**, **3b**, and **3c** are obtained in isolated yields of 50–80%, accompanied by the respective dienol thioethers **4a-4f** in 10–40% yields. When the amount of dimethyltitanocene is increased to 30.0 mmol (20–26 h), only the diolefinated compounds are obtained in 75–85% yields.

Monomethylenated products **2a-2f**, **3b**, and **3c** are conveniently purified by flash column chromatography on Florisil. Short-path vacuum distillation of compounds **2a**, **2b**, **3b**, and **2d-2f** was carried out with no observable isomerization or degradation. Similar treatment of the mixture of phenyl-substituted isomers **2c** and **3c** resulted in rearrangement to α,β-unsaturated thiolactones **6** and **7**, respectively (Scheme 2).

The more sterically constrained dienes **4d-4f** were amenable to Florisil chromatography, with little or no detectable isomerization, while the less substituted dienes **4a-4c** underwent facile rearrangement to the corresponding thiophenes **5**. Nearly quantitative conversion of dienes

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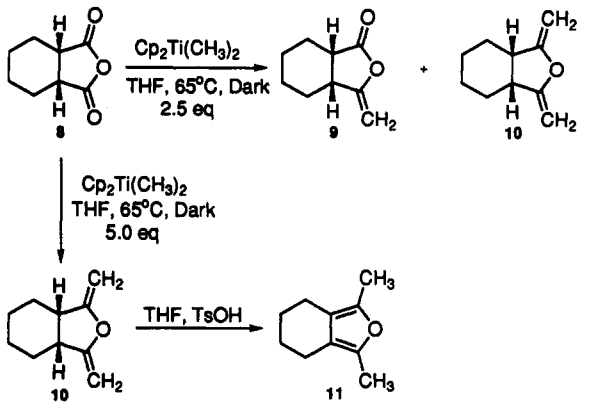
0022-3263/94/1959-0494$04.50/0

Scheme 3



4a-4e to the respective thiophenes was observed upon standing for 1 h in THF solution containing a catalytic amount of *p*-toluenesulfonic acid.[8] Isomerization was also noted for NMR samples of these dienes after 2–3 h in $CDCl_3$ solution.

Dienes **4a**, **4b**, and **4d-4f** were isolated without isomerization by short path vacuum distillation. Vacuum distillation of the phenyl-substituted diene **4c** at 65–75 °C resulted in isomerization to the thiophene **5c**, accompanied by decomposition.

Reaction of the *trans*-thioanhydride **1e** with dimethyltitanocene gave the mono- and dimethylenated products **2e** and **4e** without epimerization to the more stable *cis*-thioanhydride **1d** or cis-fused methylenation products **2d** or **4d**, respectively. Methylenation of 3-methyl- and 3-phenylsuccinic thioanhydrides **1b** and **1c** occurred with moderate chemoselectivity at the less sterically hindered carbonyls. Analogous behavior has been observed for reaction of 3-substituted succinic anhydrides with stabilized phosphorus ylides.[9]

A preliminary investigation on methylenation of five-membered ring anhydrides with dimethyltitanocene was carried out using *cis*-cyclohexane-1,2-dicarboxylic acid anhydride **8** (Scheme 3). Reaction of 6.0 mmol of anhydride **8** and 15.0 mmol of dimethyltitanocene in THF afforded enol lactone **9** and dienol ether **10** in 47 and 43% isolated yields, respectively. When dimethyltitanocene (15 mmol) was preheated at 65 °C for 1 h before addition of anhydride **8** (6 mmol), **9** and **10** were obtained in 14% and 68% respective isolated yields. However, when the reagent was preheated for longer times, its methylenating ability was greatly diminished.

Reaction of 30.0 mmol of dimethyltitanocene and 6 mmol of anhydride **8** for 22 h (without preheating the reagent) resulted in only the dienol ether **10** in 79% yield. The latter was isomerized to the corresponding dimethylfuran **11** under acidic conditions as previously indicated.

Further investigations on alkylidenation reactions of carboxylic acid anhydrides and thioanhydrides are currently under way.

Experimental Section

General Information. Melting points are uncorrected. Boiling points were obtained using short path vacuum (Kugelrohr) distillation and are uncorrected. All starting compounds and solvents were obtained from Aldrich Chemical Co. Dimethyltitanocene was prepared according to a reported procedure[10] and used as a 0.90 M solution in dry THF. Thioanhydrides **1a-1f** were prepared according to reported procedures.[11] ^1H and ^{13}C NMR were recorded at 200 and 50.3 MHz, respectively. GC analysis was performed using a 10M Hewlett-Packard HP-1 macrocapillary column. Elemental analyses were provided by Robertson Microlit Laboratories, Inc., P.O. Box 927, Madison, NJ 07940.

General Procedure for Conversion of Thiolane-2,5-diones (Succinic Thioanhydrides) to 5-Methylenethiolan-2-ones 2a-2f, 3b, and 3c. A mixture of succinic thioanhydride (6.0 mmol) in 20.0 mL of dry THF and 15.0 mmol of dimethyltitanocene (16.7 mL of a 0.90 M solution) was heated at 65 °C for 22–26 h under argon, with the exclusion of light. The course of the reaction was followed by TLC and gas chromatography. The crude product was concentrated under vacuum to a viscous brown oil and then chromatographically filtered through Florisil using 10% CH_2Cl_2/pentane as eluant. The fractions containing product were combined, concentrated, and chromatographed on Florisil using pentane to elute the dimethylenated products. The monomethylenated products were then eluted using 25% CH_2Cl_2/pentane in 50–80% yields.

5-Methylenethiolan-2-one (2a): colorless oil in 59% yield; bp 28 °C (3.4 Torr); ^1H NMR ($CDCl_3$) δ 2.75 (cm, 2 H), 2.93 (cm, J = 7.7 Hz, 2H), 5.18 (dt, J =1.9, 1.1 Hz, 1 H), 5.35 (dt, J = 1.8, 1.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 32.4, 41.9, 108.9, 144.3, 205.8.

3-Methyl-5-methylenethiolan-2-one (2b) and 4-methyl-5-methylenethiolan-2-one (3b): colorless oil in 55% combined yield; bp 27 °C (3.5 Torr). Relative yields (74:26), respectively, were determined by GC and quantitative ^{13}C and ^1H NMR. The isomers were separated on a silica gel prep plate (5% CH_2Cl_2/pentane). Isomer **2b:** ^1H NMR ($CDCl_3$) δ 1.25 (d, J = 6.8 Hz, 3H), 2.56 (ddt, J = 2.3, 2.3, 14.1 Hz, 1H), 2.83 (cm, J = 7.7, 8.8 Hz, 1 H), 3.08 (ddt, J = 1.4, 1.4, 14.1 Hz, 1 H), 5.17 (cm, J = 1.0 Hz, 1H), 5.36 (cm, J = 1.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 15.5, 41.2, 48.0, 109.1, 142.1, 208.2. Isomer **3b:** ^1H NMR ($CDCl_3$) δ 1.33 (d, J = 6.7 Hz, 3 H), 2.44 (dd, J = 7.4, 16.8 Hz, 1 H), 2.86 (dd, J = 7.8, 16.8 Hz, 1 H), 3.18 (cm, J = 1.7, 6.7 Hz, 1 H), 5.18 (dd, J = 1.3, 1.7 Hz, 1 H), 5.34 (dd, J = 1.3, 1.7 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 18.7, 39.0, 49.8, 108.1, 149.6, 204.5. Anal. Calcd for C_6H_8SO: C, 56.21; H, 6.29; S, 25.01. Found: C, 56.01; H, 5.98; S, 25.07.

5-Methylene-3-phenylthiolan-2-one (2c) and 5-Methylene-4-phenylthiolan-2-one (3c). Isomers **2c** and **3c** were obtained as a colorless oil, 65% combined yield. Relative yields (65:35), respectively, were determined by GC and quantitative ^{13}C and ^1H NMR. The isomers were separated on a silica gel prep plate (3% CH_2Cl_2/pentane). Isomer **2c:** ^1H NMR ($CDCl_3$) δ 3.11 (ddd, J = 1.8, 8.0, 15.0 Hz, 1 H), 3.34 (ddd, J = 1.8, 8.0, 15.0 Hz, 1 H), 3.97 (dd, J = 8.0, 8.4 Hz, 1 H), 5.27 (dd, J = 1.1, 1.8 Hz, 1 H), 5.46 (dd, J = 1.1, 1.8 Hz, 1 H), 7.24–7.41 (cm, 5H); ^{13}C NMR ($CDCl_3$) δ 41.2, 58.5, 109.5, 127.6, 127.7, 128.8, 137.2, 142.1, 205.3. Isomer **3c:** ^1H NMR ($CDCl_3$) δ 3.00 (dd, J = 8.5, 17.0 Hz, 1 H), 3.12 (dd, J = 8.2, 17.0 Hz, 1 H), 4.28 (dddd, J= 2.3, 2.0, 8.5, 8.2 Hz, 1 H), 5.07 (dd, J = 1.4, 2.0 Hz, 1 H), 5.26 (dd, J = 1.4, 2.3 Hz, 1 H), 7.27–7.37 (cm, 5 H); ^{13}C NMR* ($CDCl_3$) δ 49.6, 49.9, 110.9, 128.8, 139.3, 147.8, 203.3. Anal. Calcd for $C_{11}H_{10}SO$: C, 69.44; H, 5.29; S, 16.85. Found: C, 69.60; H, 4.99; S, 16.56. *The ^{13}C spectrum was obtained on a mixture of **2c** and **3c**. Total assignment of aromatic carbon peaks was not possible.

***cis*-9-Methylene-8-thiabicyclo[4.3.0^{1,6}]nonan-7-one (2d):** colorless oil; 79% yield; bp 50 °C (3.4 Torr); ^1H NMR ($CDCl_3$) δ 1.24–1.44 (cm, 4 H), 1.61–1.74 (cm, 2 H), 2.01–2.04 (cm, 2 H), 2.83 (ddd, J = 5.2, 5.2, 6.4 Hz, 1 H), 3.05 (cm, 1H), 5.16 (dd, J = 1.1, 1.1 Hz, 1 H), 5.36 (dd, J = 1.1, 1.1 Hz, 1 H); spin connectivity determined by COSY; ^{13}C NMR ($CDCl_3$) δ 22.5, 23.0, 23.66, 28.3, 45.4, 53.3 108.3, 147.2, 206.5. Anal. Calcd for $C_9H_{12}SO$: C, 64.24; H, 7.18; S, 19.05. Found C, 63.99; H, 7.08; S, 19.35.

***trans*-9-Methylene-8-thiabicyclo[4.3.0^{1,6}]nonan-7-one (2e):** colorless oil; 66% yield; ^1H NMR ($CDCl_3$) δ 1.13–1.51 (cm,

(8) Acid catalyzed isomerization of dienol thioethers and dienol ethers obtained by reaction of corresponding five-membered ring thioanhydrides and anhydrides with stabilized phosphorus ylides have been observed by Flitsch *et al.* and Babidge *et al.* in refs 3 and 2a, respectively.

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4 H), 1.85–1.94 (cm, 2 H), 2.16–2.29 (cm, 3 H), 2.41 (cm, 1 H), 5.15 (dd, J = 1.2, 2.4 Hz, 1 H), 5.29 (dd, J = 1.2, 2.3 Hz, 1 H); spin connectivity determined by COSY; ^{13}C NMR ($CDCl_3$) δ 25.0, 25.1, 26.5, 28.3, 49.5, 57.2, 106.2, 146.8, 205.1. Anal. Calcd for $C_9H_{12}SO$: C, 64.24; H, 7.18; S, 19.05. Found: C, 64.09; H, 7.32; S, 18.85.

***cis*-4-Methylene-3-thiabicyclo[3.2.0^{1,5}]heptan-2-one (2f):** colorless oil; 53% yield; bp 36 °C (3.9 Torr); ^{1}H NMR ($CDCl_3$) δ 2.26 (cm, 2 H), 2.52 (cm, 2 H), 3.37 (cm, 1 H), 3.68 (cm, 1 H), 5.13 (t, J = 1.2 Hz, 1 H), 5.19 (t, J = 1.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 24.1, 27.5, 43.3, 51.7, 107.3, 148.8, 209.1. Anal. Calcd for C_7H_8SO: C, 59.96; H, 5.75; S, 22.86. Found: C, 60.34; H, 6.02; S, 22.69.

***cis*-9-Methylene-8-oxabicyclo[4.3.0^{1,6}]nonan-7-one (9).** Reaction of anhydride 8 with dimethyltitanocene was carried out and isolated under conditions similar to those described above for monomethylenation of thiolane-2,5-diones: colorless oil; 47% yield; ^{1}H NMR ($CDCl_3$) δ 1.22–2.00 (cm, 8 H), 2.79 (cm, 1 H), 3.00 (cm, 1 H), 4.34 (dd, J = 1.2, 2.5 Hz, 1 H), 4.72 (dd, J = 1.2, 2.4 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 22.2, 22.3, 22.8, 27.5, 38.2, 39.9, 87.6, 158.8, 175.9. The ^{1}H NMR data are in agreement with literature values.[12]

General Procedure for Conversion of Thiolane-2,5-diones (Succinic Thioanhydrides) to 2,5-Dimethylenethiolanes 4a-4f. A mixture of the succinic thioanhydride (6.0 mmol) in 20.0 mL of dry THF and 30.0 mmol of dimethyltitanocene (33.3 mL of 0.90 M solution) was heated at 65 °C for 20–26 h under argon, with the exclusion of light. The progress of the reaction was followed by TLC and gas chromatography. The crude product was concentrated to a viscous brown oil under vacuum at rt.

2,5-Dimethylenethiolane (4a). Compound **4a** was obtained as a colorless oil by short path distillation of the crude product: bp 25 °C (5.0 Torr); ^{1}H NMR ($CDCl_3$) δ 2.69 (cm,* 4 H), 4.94 (cm,* 1 H), 5.09 (cm,* 1 H), *high order multiplet due to symmetry; ^{13}C NMR ($CDCl_3$) δ 36.8, 103.2, 155.3. Chromatography of the crude **4a** on Florisil (100% pentane) resulted in isomerization to 2,5-dimethylthiophene **5a**[13] in 40% yield.

3-Methyl-2,5-dimethylenethiolane (4b). Compound **4b** was obtained as a colorless oil by short path distillation: bp 29 °C (3.5 Torr); ^{1}H NMR (C_6D_6) δ 0.89 (d, J = 6.7 Hz, 3 H), 2.02 (ddt, J = 1.8, 7.7, 13.5 Hz, 1 H), 2.39 (ddt, J = 1.6, 6.9, 13.5 Hz, 1 H), 2.50 (cm, 1 H), 4.86 (cm, J = 1.7 Hz, 1 H), 4.91 (cm, J = 1.6, 1.7 Hz, 2 H), 4.98 (cm, J = 1.6, 1.8 Hz, 1 H); ^{13}C NMR (C_6D_6) δ 18.4, 42.7, 45.4, 102.6, 103.9, 148.0 154.9. Anal. Calcd for $C_7H_{10}S$: C, 66.61; H, 7.98; S, 25.40. Found: C, 66.89; H, 8.01; S, 25.05. Chromatography of the crude **4b** on Florisil (100% pentane) afforded 2,3,5-trimethylthiophene **5b** in 75% yield.

2,5-Dimethyl-3-phenylthiophene (5c). Chromatography of crude dimethylenethiolane **4c** on Florisil (100% pentane) afforded dimethylthiophene **5c** as a colorless oil in 78% yield: bp 65 °C (3.5 Torr); ^{1}H NMR ($CDCl_3$) δ 2.44 (s, 3 H), 2.45 (s, 3 H), 6.70 (s, 1 H), 7.27–7.41 (cm, 5 H); ^{13}C NMR ($CDCl_3$) δ 13.9, 14.9, 127.1 (C_4, Determined by HETCOR), 126.3, 128.1, 128.4, 131.5, 135.3, 136.8, 138.1. Anal. Calcd for $C_{12}H_{12}S$: C, 76.54; H, 6.42; S, 17.02. Found: C, 76.30; H, 6.55; S, 16.93.

***cis*-7,9-Dimethylene-8-thiabicyclo[4.3.0^{1,6}]nonane (4d).** Chromatography of the crude product on Florisil (100% pentane) afforded **4d** in 84% yield: colorless oil; bp 38.5 °C (3.3 Torr); ^{1}H NMR ($CDCl_3$) δ 1.23–1.73 (cm, 8 H), 2.89 (cm, 2 H), 4.97 (m, 1 H), 5.05 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 22.7, 26.9, 47.8, 108.4, 150.7; MS (EI, 70 eV) m/z 166 (M^+, 100), 151 (73), 138 (53), 125 (15). Anal. Calcd for $C_{10}H_{14}S$: C, 72.23; H, 8.48; S, 19.28. Found: C, 72.50; H, 8.23; S, 18.89. Isomerization of **4d** with toluenesulfonic acid (cat.) in THF afforded the corresponding dimethylthiophene **5d**, which gave ^{1}H NMR data in agreement with literature values.[14]

***trans*-7,9-Dimethylene-8-thiabicyclo[4.3.0^{1,6}]nonane (4e).** Chromatography of the crude product on Florisil (100% pentane) gave **4e** as a colorless oil in 81% yield: ^{1}H NMR ($CDCl_3$) δ 1.26 (cm, 4 H), 1.87 (cm, 2 H), 2.04 (cm, 2 H), 2.15 (cm, 2 H), 4.96 (cm, 2 H), 5.00 (cm, 2 H); ^{13}C NMR ($CDCl_3$) δ 25.7, 29.4, 52.1, 101.3, 151.6. Isomerization of **4e** with toluenesulfonic acid (cat.) in THF afforded dimethylthiophene **5d**.

***cis*-2,4-Dimethylene-3-thiabicyclo[3.2.0^{1,5}]heptane (4f).** Chromatography of the crude product on Florisil (100% pentane) afforded **4f** in 74% yield: pale yellow oil; bp 36 °C (4.2 Torr); ^{1}H NMR ($CDCl_3$) δ 2.09 (cm,* 2H), 2.43 (cm,* 2 H), 3.60 (cm,* 2 H), 4.98 (cm,* 2 H), 5.00 (cm,* 2 H), *high order multiplet due to symmetry; ^{13}C NMR ($CDCl_3$) δ 27.3, 47.9, 102.3, 154.1.

***cis*-7,9-Dimethylene-8-oxabicyclo[4.3.0^{1,6}]nonane (10).** Reaction of anhydride 8 with dimethyltitanocene was carried out under similar conditions to those described for dimethylenation of thiolane-2,5-diones. Chromatography of crude product on Florisil (100% pentane) afforded **10** as a colorless oil in 79% yield: ^{1}H NMR ($CDCl_3$) δ 1.36 (cm, 2 H), 1.44–1.75 (cm, 6 H), 2.75 (cm, 2 H), 3.99 (dd, J = 1.1, 1.9 Hz, 2 H), 4.40 (dd, J = 1.1, 1.9 Hz, 2 H); ^{13}C NMR (C_6D_6) δ 23.1, 26.9, 40.3, 82.1, 164.1. Isomerization of **10** with toluenesulfonic acid (cat.) in THF afforded the corresponding dimethylfuran **11**, which gave ^{1}H NMR data in agreement with literature values.[15]

Acknowledgment. We thank Dr. Walter Boyko, Director of the NMR Laboratory, Villanova University, for his insightful help with interpretation of NMR spectra.

Supplementary Material Available: ^{13}C NMR spectra of **10**, **2a**, **4a**, and **4f** (4 pages). This material is contained in libraries on microfiche, immediately follows this article in the microflim version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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