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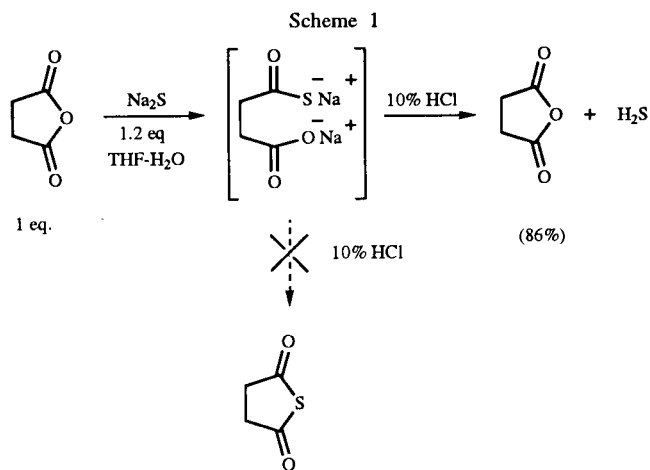
Reaction of five-membered ring anhydrides with sodium sulfide has previously been employed for synthesis of the corresponding thioanhydrides in low yields. Re-examination of the stoichiometry reveals reaction of cyclic anhydride with sodium sulfide (2:1 respectively), affords the thioanhydride accompanied by the corresponding dicarboxylate in a 1:1 molar ratio. The mechanistic pathway for this reaction has also been elucidated. Optimization of reaction conditions has resulted in the synthesis of a variety of four to seven-membered ring thioanhydrides in yields approaching theoretical.

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One aspect of our ongoing research involves the synthesis of oxygen and sulfur heterocycles containing exocyclic carbon-carbon double bonds α to the heteroatoms. In conjunction with this interest, we recently reported results of a study on the mono- and bis-carbonyl methylenation of various five-membered ring thioanhydrides [2].

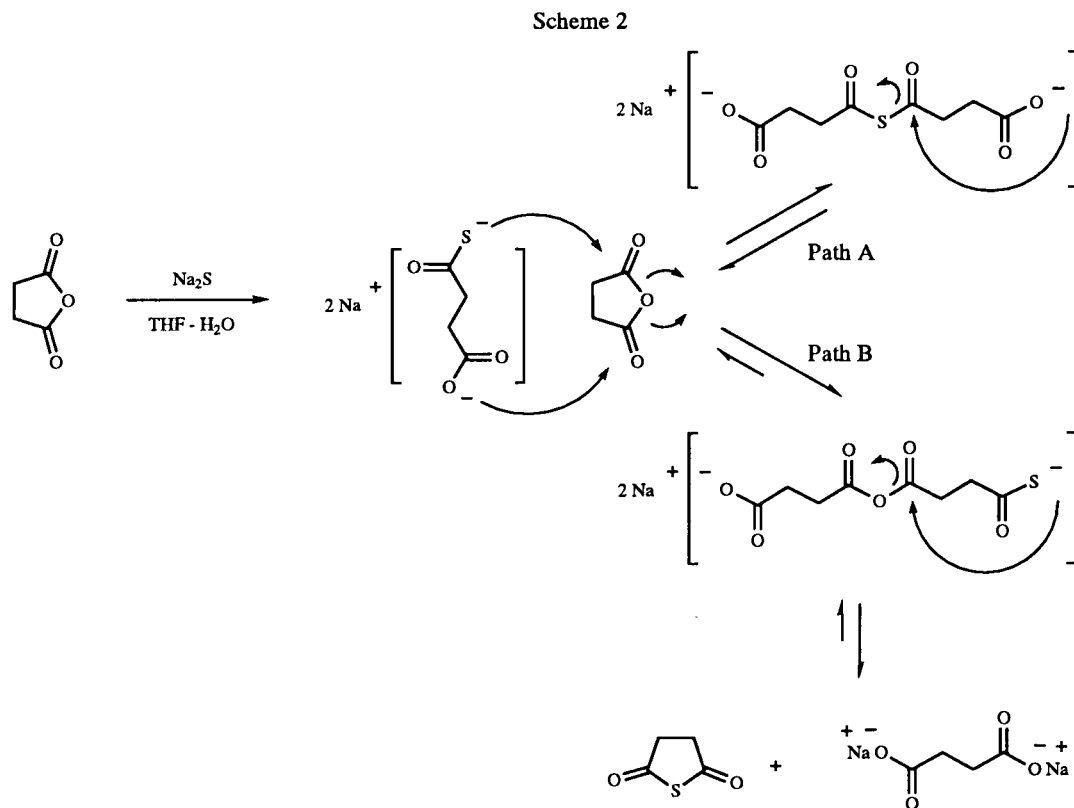
The thioanhydrides were conveniently obtained, although in quite low yields, by the method of Reissert and Holle [3-9], involving trituration of the corresponding cyclic anhydrides with sodium sulfide nonahydrate *neat* in a 1:1.2 molar ratio, respectively, followed by aqueous hydrochloric acid workup. In all cases, we found the thioanhydrides to be accompanied by starting anhydrides (20-50%), as well as intractable materials. While cyclic thioanhydrides have been obtained alternately in moderate yields by a few other methods, mainly by reaction of acid chlorides of 1,2-dicarboxylic acids with potassium or pyridinium hydrosulfides [10-14], the ease of formation of cyclic anhydrides, and their subsequent reaction with sodium sulfide prompted us to further investigate this method of thioanhydride formation in order to optimize yields.

It has previously been assumed that formation of succinic-type thioanhydrides occur *via* ring opening of the anhydrides by hydrosulfide ion to form the corresponding sodium monothiosuccinates, which upon acidification, undergo ring closure [3]. Not surprisingly, we observe that reaction of succinic anhydride (1.0 molar equivalent) with sodium sulfide (1.2 molar equivalents) in tetrahydrofuran-water rather than *neat*, at 20°, gives only sodium monothiosuccinate. However, upon acidification with 10% hydrochloric acid, succinic anhydride was obtained in 86% yield, accompanied by hydrogen sulfide (Scheme 1). No thioanhydride was formed under these reaction conditions. This result is in agreement with a report by Marvel and Kraiman [15], noting that acidification of sodium monothiophthalate resulted in phthalic anhydride and hydrogen sulfide. This result also explains the origin of the anhydrides, observed as contaminants in all five-membered ring thioanhydrides which we prepared [2], but does not account for the formation of thioanhydrides using the Reissert-Holle procedure.



When the reaction was repeated using excess succinic anhydride with sodium sulfide (1.2:1.0 molar ratio, respectively), 0.2 molar equivalent of succinic thioanhydride was formed *prior to acidification*. This strongly suggests that thioanhydride is formed by reaction of anhydride with the intermediate monothiosuccinate, generating the mixed acyclic anhydride (Scheme 2, Path B), followed by ring closure *via* intramolecular attack of the thiocarboxylate. This was further supported by reaction of succinic anhydride with sodium sulfide in 2:1 molar ratio, which afforded ~1.0 molar equivalent each of succinic thioanhydride and sodium succinate. The correct stoichiometry for cyclic thioanhydride formation is thus shown in Scheme 3.

Due to the higher nucleophilicity of the thiocarboxylate relative to the carboxylate moiety, formation of the acyclic thioanhydride (Scheme 2, Path A) should be kinetically favored over the corresponding acyclic anhydride (Path B). Thus, in order for succinic thioanhydride to be formed *via* Path B, acyclic thioanhydride formation must be reversible. To further examine this possibility, reaction of methylsuccinic anhydride and sodium sulfide (1.0 molar equivalent each) in tetrahydrofuran-water, was followed by addition of succinic anhydride (1.0 molar equivalent), resulting in a 1:1 mixture of succinic and

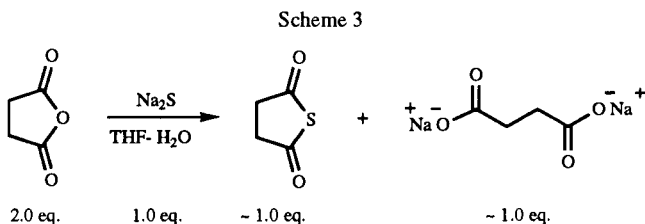


methylsuccinic thioanhydrides (Scheme 4). The formation of succinic thioanhydride is consistent with formation of the acyclic thioanhydride intermediate, followed by reversion to methylsuccinic anhydride and monothiosuccinate.

As noted above, reaction of equimolar amounts of succinic anhydride and sodium sulfide in tetrahydrofuran-water provided only sodium monothiocarboxylate. This indicates that initial reaction of the anhydride with sodium sulfide is faster than the subsequent reaction of the anhydride with monothiosuccinate. The success of the Reissert-Holle procedure in providing thioanhydrides,

thioanhydride. Additionally, reaction of excess sodium sulfide with cyclic thioanhydride could result in ring opening to the corresponding bithiocarboxylate. Acidification of the bithiocarboxylate intermediate would result in re-formation of the thioanhydride and hydrogen sulfide [10].

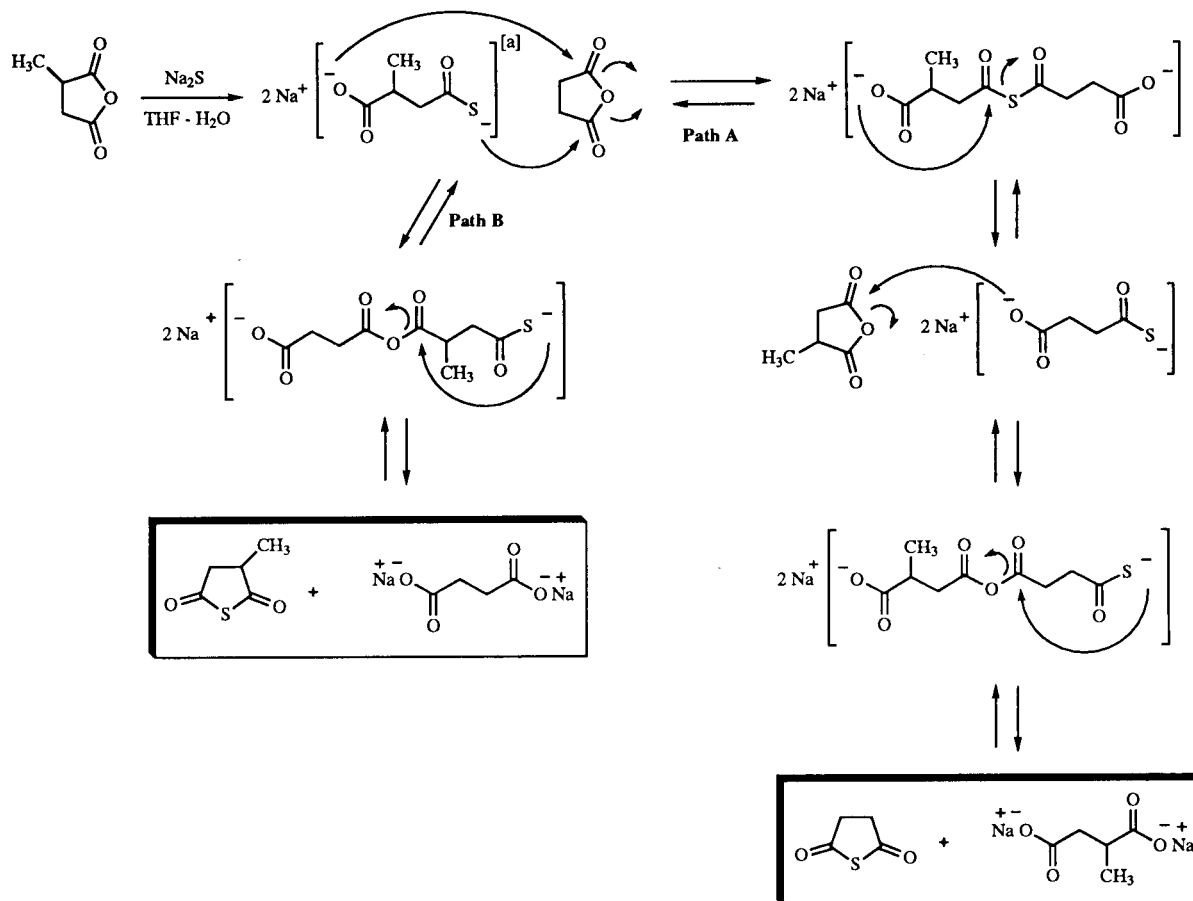
Reaction of a variety of five-membered ring anhydrides with sodium sulfide in 2:1 molar ratio, respectively, in tetrahydrofuran-water has provided the corresponding thioanhydrides shown in Table 1. In general, yields approaching theoretical were obtained, based on moles of sodium sulfide, with nearly complete recovery of the corresponding 1,2-diacids. The starting anhydrides were obtained essentially quantitatively by reaction of the respective diacids with *N*-methylmorpholine and methylchloroformate in anhydrous tetrahydrofuran [16]. Removal of the *N*-methylmorpholine hydrochloride by filtration, followed by addition of aqueous sodium sulfide to the filtrate gave the corresponding cyclic thioanhydride in a one-pot procedure (Scheme 5). After extraction of the thioanhydride with ether, the aqueous solution containing the sodium salt of the diacid was acidified to permit facile recovery of the diacid.



albeit in low yields, is apparently due to the heterogeneity of the reaction mixture resulting from trituration of anhydride with neat sodium sulfide. Under these conditions, monothiosuccinate is formed in the presence of anhydride, from which reaction can occur to form cyclic

Reaction of the anhydride congeners of thioanhydrides **9**, **10** and **11** with sodium sulfide in tetrahydrofuran-water gave significantly lower yields of thioanhydrides than the

Scheme 4



[a] The regioisomer 2-methylmonothiosuccinate would afford identical products.

other cases listed in Table 1. Furthermore, the crude thioanhydrides were contaminated with starting anhydrides. In each case the mole ratio of anhydride to thioanhydride remained constant, regardless of reaction time, suggesting equilibrium between them. To examine this possibility, equimolar amounts of *endo*-bicyclo-[2.2.1]hept-5-ene-2,3-dicarboxylic thioanhydride **9** and the sodium salt of the corresponding 2,3-dicarboxylic acid were co-dissolved in tetrahydrofuran-water at 20° and monitored by gas chromatography. Thioanhydride **9** and the corresponding anhydride were observed, reaching equilibrium in 20 minutes (91:9 relative % respectively, determined by quantitative ^1H and ^{13}C nmr). This result is consistent with the mechanistic pathway shown in Scheme 2, assuming that all steps are reversible. Equilibrium between thioanhydride and starting anhydride, coupled with a gradual loss of anhydride due to hydrolysis would, of course, result in lower yields of thioanhydride. A dramatic improvement in yields of the *exo*-thioanhydrides **10** and **11** (less for *endo*-thioanhydride **9**) occurred when the reactions were carried out under

phase-transfer conditions using cetyltrimethylammonium bromide, (tetrabutylammonium iodide was used to synthesize compounds **10** and **20**) in methylene chloride-water. In general, however, the five-membered ring thioanhydrides shown in Table 1 were obtained in high yields using either tetrahydrofuran-water or under phase-transfer conditions. No epimerization was observed for thioanhydrides **4**, **5**, **6**, **7** or **8**. Reaction of maleic, 2,3-dimethylmaleic, and 2,3-diphenylmaleic anhydrides with sodium sulfide by either method failed to give tractable products, possible due to Michael-type addition of sulfide ion with attendant polymerization [17].

Various four, six and seven-membered ring anhydrides have also been synthesized from the appropriate diacids using *N*-methylmorpholine and methylchloroformate, then subjected to *in situ* reaction with sodium sulfide in tetrahydrofuran-water to form the respective cyclic thioanhydrides (Table 2), although in somewhat lower yields. This was not surprising, since hydrolysis of the starting and/or intermediate acyclic anhydrides, would be expected to compete with decreased rates of cyclization for thioanhy-

Table 1

Diacid/Anhydride	Thioanhydride	% Yield [a,c]	% Yield [b,c]
R = R' = H	R = R' = H	1	99
R = CH ₃ , R' = H	R = CH ₃ , R' = H	2	96
R = Ph, R' = H	R = Ph, R' = H	3	95
R = R' = CH ₃	R = R' = CH ₃	4 (<i>Meso</i>)	95
R = R' = CH ₃	R = R' = CH ₃	5 (<i>R,S</i>)	96
		6	99
		7	98
		8	92
		9	80
		10	74
		11	83
		12	99

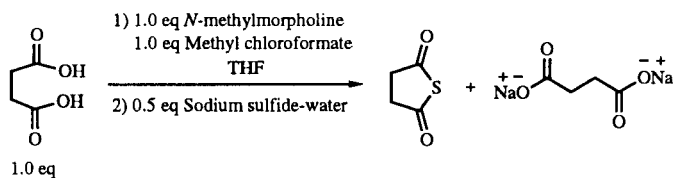
[a] Method A.

[b] Method B.

[c] Isolated yields based on moles of sodium sulfide.

drides of these ring sizes. In order to minimize hydrolysis, the latter reactions were also carried out under phase-transfer conditions, resulting in greatly improved yields.

Scheme 5



Disubstituted four-membered ring thioanhydrides such as **23** and **24** were previously obtained by Williams, Van Saun, and Schauble [11,18] by reaction of the corresponding acid chlorides with hydrogen sulfide in pyridine to furnish the pyridinium bithiocarboxylates, which were oxi-

Table 2

Diacid/Anhydride	Thioanhydride	% Yield [a,c]	% Yield [b,c]
		13	80
		14	84
		15	71
		16	84
		17	81
		18	21
		19	77
		20	92
		21	95
		22	66
		23	74
		24	81

[a] Method A.

[b] Method B.

[c] Isolated yields based on moles of sodium sulfide.

dized to the corresponding cyclic diacyldisulfides, followed by sulfur extrusion using triphenylphosphine. Attempts to prepare monosubstituted four-membered ring thioanhydrides by this route, or *via* reaction of cyclic anhydrides with sodium sulfide have not been successful. The ease of preparation of disubstituted four-membered ring thioanhydrides using anhydride-sodium sulfide methodology, coupled with their facile thermolysis (loss of carbonyl sulfide) at temperatures above 145°, [18] makes them convenient precursors to disubstituted ketenes.

Six-membered ring thioanhydrides have not been reported previously, except for glutaric thioanhydride **13**, obtained in ~2% yield *via* the Reissert-Holle procedure [12], and 1,8-naphthalic thioanhydride, obtained by isomerization of the mono-thioanhydride [19]. In the present study, six-membered ring thioanhydrides **13-17** were all obtained in excellent yields under phase-transfer conditions. However, spiro-thioanhydride **18** was isolated in only 35% yield, with as much as ~50 mole % of the starting anhydride, observed in the crude product. This result again appears to be due to equilibrium between thioanhydride and starting anhydride, which in this case favors the latter. Lower yields of **13-18** were obtained in tetrahydrofuran-water, due to lack of solubility of starting anhydrides and intermediate salts, as well as competition of anhydride hydrolysis with thioanhydride formation.

Seven-membered ring thioanhydrides are essentially unknown in the literature, except for diphenic thioanhydride **19** reported as a minor product from the synthesis of the bithioacid, and the 4,5-dihydro-5,5-dimethyl-2-benzothiepine-1,3-dione, obtained from carbonyl sulfide insertion with benzonickelacyclopentene complex [20,21]. The parent seven-membered ring (adipic) anhydride could not be obtained by simple dehydration procedures, but is accessible *via* thermal depolymerization of polymeric anhydride [22]. Reaction of adipic anhydride with sodium sulfide (1.0:2.0 molar ratio) in tetrahydrofuran-water gave no tractable product; however, the thioanhydride of benzene-1,2-diacetic acid **20**, for which seven-membered ring formation is expected to be more entropically favored due to the planar benzene ring, is obtained in 92% yield. The diphenic thioanhydride **19**, in which two phenyl groups, are expected to be somewhat out of plane to each other also provides a sufficient degree of conformational constraint to permit seven-membered ring formation. Likewise, thioanhydride **21** was obtained in high yield. In the latter case, formation of the cyclic thioanhydride is apparently favored over acyclic product(s) due to the conformational constraint (60° dihedral angle) resulting from the *trans* ring fusion to the six-membered ring.

EXPERIMENTAL

Melting points are uncorrected. Boiling points were obtained using short path vacuum (Kugelrohr) distillation and are uncor-

rected. All starting compounds and solvents were obtained from Aldrich Chemical Co. Although sodium sulfide nonahydrate may be used, anhydrous sodium sulfide generally gave higher yields and was used in all cases described herein. Gas chromatographic analyses were performed using a 10 meter Hewlett-Packard HP-1 macrocapillary column. Thin layer chromatography was performed on silica gel, using 100% methylene chloride as eluant. Elemental analyses were provided by Robertson Microlit Laboratories Inc., Madison, NJ. Yields for cyclic thioanhydrides (**1-24**) are listed in Tables 1 and 2.

The ¹H and ¹³C nmr spectra were recorded on a Varian Associates XL-200 instrument at 200 and 50.3 MHz respectively, in chloroform-*d* using tetramethylsilane as the internal standard.

General Procedure for Conversion of Dicarboxylic Acids to Cyclic Thioanhydrides (**1-8**, **12-17**, and **20-24**).

Preparation of Cyclic Anhydrides.

A solution of the appropriate diacid and *N*-methylmorpholine (20 mmoles each) in 50.0 ml of dry tetrahydrofuran at 0° under argon was prepared in a flame dried 250 ml round-bottom flask. Compounds **14** and **15** were prepared in acetone rather than THF. To this solution, 20.0 mmoles of methyl chloroformate was added, dropwise over 5 minutes. The resulting mixture was stirred for 15 minutes at 20° (1.0-1.5 hours for six and seven-membered rings), monitored by tlc and filtered to remove *N*-methylmorpholine hydrochloride.

Conversion of Cyclic Anhydrides to Thioanhydrides.

Method A.

The filtrate, containing the freshly prepared anhydride (20 mmoles) in THF was then treated with sodium sulfide (10.0 mmoles) in 15.0 ml of water. The resulting mixture was stirred for 10-30 minutes (monitored by tlc and gc), poured into 50 ml of ethyl ether and separated. The aqueous phase was extracted with ethyl ether (2 x 25 ml). The combined ether extract was washed with water, saturated sodium bicarbonate and brine (50 ml each), dried (magnesium sulfate), and evaporated under reduced pressure to afford the crude thioanhydride. Some crude thioanhydrides obtained in this manner (or by method B) were nearly analytically pure. Saturation of the aqueous phase with sodium chloride, followed by acidification (6*M* hydrochloric acid) and ether extraction resulted in recovery of nearly pure starting diacid.

Method B.

The filtrate, containing the freshly prepared anhydride (20 mmoles) was evaporated to dryness under reduced pressure at 20°. To the anhydride was added 50 ml of methylene chloride, 50 mg of cetyltrimethylammonium bromide (tetrabutylammonium iodide was used for compounds **10** and **20**) and sodium sulfide (10 mmoles) in 50 ml of water. Reactions required 2-6 hours for completion and were easily monitored by removing aliquots from the organic phase and analyzing the mixture by pmr, gc and tlc. When reaction was complete, the aqueous phase was separated and extracted with an additional 50 ml of methylene chloride. The combined methylene chloride extract was washed with water, saturated sodium bicarbonate and brine (25 ml each), dried (magnesium sulfate), and evaporated under reduced pressure, affording crude thioanhydride.

Thiolane-2,5-dione (1).

The crude product was obtained as a pale yellow oil, bp 95° (3.5 torr), one component by gc, crystallized to white needles, mp 26.5-27°; ¹H nmr: δ 3.10 (s, 4H); ¹³C nmr: δ 40.4 (C-3, 4), 200.6 (C-2, 5) [3-9].

Anal. Calcd. for C₄H₄SO₂: C, 41.38; H, 3.48; S, 27.56. Found: C, 41.26; H, 3.56; S, 27.24.

R,S-3-Methylthiolane-2,5-dione (2).

The crude pale yellow oil, one component by gc, was distilled, bp 89-90° (3.5 torr); ¹H nmr: δ 1.41 (d, 3 H, J = 6.7 Hz, -CH₃), 2.74 (cm*, 1 H, H-4), 3.23 (cm*, 2 H, H-4, H-3); *High order ABDX₃; ¹³C nmr: δ 16.2 (-CH₃), 47.6 (C-4), 48.5 (C-3), 199.3 (C-5), 203.5 (C-2) [23, 24].

Anal. Calcd. for C₅H₆SO₂: C, 46.15; H, 4.65; S, 24.59. Found: C, 46.43; H, 4.94; S, 24.72.

R,S-3-Phenylthiolane-2,5-dione (3).

The crude product was distilled affording a yellow oil, bp 170° (3.5 torr); ¹H nmr: δ 3.27 (dd, 1 H, J = 5.7, 18.0 Hz, H-4_a), 3.54 (dd, 1 H, J = 9.0 Hz, H-4_b), 4.40 (dd, 1 H, H-3), 7.35 (m, 5 H, Ph); ¹³C nmr: δ 48.4 (C-4), 57.8 (C-3), 127.0, 127.2, 128.1, 128.3, 129.0, 135.6 (Ph), 198.9 (C-5), 200.5 (C-2) [25].

Anal. Calcd. for C₁₀H₈SO₂: C, 62.49; H, 4.20; S, 16.65. Found: C, 62.56; H, 4.32; S, 16.45.

meso-3,4-Dimethylthiolane-2,5-dione (4).

The crude thioanhydride was distilled as a colorless oil, bp 119° (3.2 torr), crystallized to white needles, mp 73.5-74.5°; ¹H nmr: δ 1.29 (cm*, 6H, CH₃), 3.24 (cm*, 2H, H-3, 4), *High order; ¹³C nmr: δ 11.6 (CH₃), 51.2 (C-3, 4), 202.5 (C-2, 5) [6].

Anal. Calcd. for C₆H₈SO₂: C, 49.99; H, 5.60; S, 22.20. Found: C, 50.36; H, 5.54; S, 22.26 (Elemental analyses were performed on a mixture of *meso* and *R,S* isomers).

R,S-3,4-Dimethylthiolane-2,5-dione (5).

The crude product was distilled as a colorless oil, bp 135° (3.2 torr), crystallized to white solid, mp 80-81°; ¹H nmr: δ 1.39 (cm*, 6H, CH₃), 2.81 (cm*, 2H, H-3, 4), *High order; ¹³C nmr: δ 14.2 (CH₃), 54.9 (C-3, 4), 201.7 (C-2, 5) [6].

cis-Bicyclo[4.3.0.1⁶]-8-thionane-7,9-dione (6).

The crude product was distilled as a colorless oil, bp 118° (3.5 torr); ¹H nmr: δ 1.48 (cm, 4 H, H-3, 4), 1.87 (cm, 4 H, H-2, 5), 3.15 (cm, 2 H, H-1, 6); ¹³C nmr: δ 22.8 (C-3, 4), 25.3 (C-2, 5), 53.3 (C-1, 6), 202.1 (C-7, 9); ms: (EI, 70 eV) *m/z* 170 (M⁺, 6), 110 (1), 82 (100), 67 (89), 54 (85). The pmr data are in agreement with literature values [12].

Anal. Calcd. for C₈H₁₀SO₂: C, 56.44; H, 5.92; S, 18.83. Found: C, 55.99; H, 6.07; S, 18.89 (Elemental analyses was performed on a mixture of *cis* and *trans* isomers).

trans-Bicyclo[4.3.0.1⁶]-8-thionane-7,9-dione (7).

This compound was obtained as a white solid without further purification, mp 101-101.5°; ¹H nmr: δ 1.24 (cm, 2H, H_a-2, 5), 1.44 (cm, 2H, H_a-3, 4), 1.94 (cm, 2 H, J = 8.5 Hz, H_e-3, 4), 2.38 (cm, 2 H, J = 13.0 Hz, H_e-2, 5), 2.66 (cm, 2H, H-1, 6); ¹³C nmr: δ 25.0 (C-3, 4), 26.3 (C-2, 5), 57.4 (C-1, 6), 199.6 (C-7, 9); ms: (EI, 70 eV) *m/z* 170 (M⁺, 6), 110 (2), 82 (100), 67 (92), 54 (82). The pmr data are in agreement with published values [12].

cis-Bicyclo[3.2.0.1⁵]-3-thiepane-2,4-dione (8).

This compound was distilled to afford a colorless oil, bp 109° (4.0 torr); ¹H nmr: δ 2.34 (cm, 2H, H-6, 7), 2.69 (cm, 2H, H-6, 7), 3.64 (cm, 2H, H-1, 5); ¹³C nmr: δ 31.8 (C-6, 7), 58.5 (C-1, 5), 211.5 (C-2, 4). The pmr data are in agreement with literature values [12].

Anal. Calcd. for C₆H₆SO₂: C, 50.70; H, 4.26; S, 22.51. Found: C, 50.70; H, 4.24; S, 22.43.

endo-Bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic Thioanhydride (9).

This compound was obtained as white needles from pentane-methylene chloride, mp 133-134° (lit 134-135°); ¹H nmr: δ 1.58 (cm, 1H, J = 0.6, 1.4 Hz, H-7_a), 1.72 (cm, 1H, J = 1.8 Hz, H-7_b), 3.46 (cm*, 2H, H-1, 4), 3.73 (cm*, 2H, H-2, 3), 6.25 (cm*, 2H, H-5, 6), *High order; ¹³C nmr: δ 47.2 (C-1, 4), 52.3 (C-7), 58.7 (C-2, 3), 133.9 (C-5, 6), 202.2 (C=O). Spectral data are in agreement with literature values [5].

Anal. Calcd. for C₉H₈SO₂: C, 59.98; H, 4.47; S, 17.79. Found: C, 60.21; H, 4.13; S, 17.95.

exo-7-Oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic Thioanhydride (10).

The crude product was obtained as white needles from ethyl acetate, mp 71-72° (lit 72-73°); ¹H nmr: δ 3.29 (s, 2H, H-2, 3), 5.37 (cm*, 2H, J = 2 Hz, H-1, 4), 6.56 (cm*, 2H, H-5, 6), *High order; ¹³C nmr: δ 60.2 (C-2, 3), 83.3 (C-1, 4), 137 (C-5, 6), 200.1 (C=O).

Anal. Calcd. for C₈H₆SO₃: C, 52.75; H, 3.32; S, 17.57. Found: C, 52.55; H, 2.94; S, 17.62. Spectral data are consistent with literature values [26].

exo-7-Oxabicyclo[2.2.1]heptane-2,3-dicarboxylic Thioanhydride (11).

Crude 11 was obtained as white needles (pentane-ether), mp 78-79° (lit 79-80°); ¹H nmr: δ 1.60-1.87 (cm*, 4H, H-5, 6), 3.24 (s, 2H, H-2, 3), 5.00 (cm*, 2H, J = 5.6 Hz, H-1, 4), *High order; ¹³C nmr: δ 28.3 (C-5, 6), 62.1 (C-2, 3), 80.8 (C-1, 4), 202.1 (C=O).

Anal. Calcd. for C₈H₈SO₃: C, 52.17; H, 4.38; S, 17.37. Found: C, 52.41; H, 3.99; S, 17.51. Spectral data is consistent with literature values [7,8].

Phthalic Thioanhydride (12).

This compound was obtained as a white solid without further purification, mp 112-113° (lit 115°); ¹H nmr: δ 7.89 (cm, Ph); ¹³C nmr: δ 123.5, 134.8, 138.4 (Ph), 189.5 (C=O) [3].

Anal. Calcd. for C₈H₄SO₂: C, 58.52; H, 2.45; S, 19.52. Found: C, 58.26; H, 2.13; S, 19.22.

Thiane-2,6-dione (Glutaric Thioanhydride) (13).

This compound was distilled as a colorless oil, bp 106-107° (2.0 torr), crystallized to white solid, mp 43-44°; ¹H nmr: δ 2.17 (m, 2H, H-4), 2.81 (m, 4H, H-3, 5); ¹³C nmr: δ 18.5 (C-4), 40.3 (C-3, 5), 197.7 (C-2, 6). The pmr data are in agreement with literature values [12].

Anal. Calcd. for C₅H₆SO₂: C, 46.13; H, 4.64; S, 24.63. Found: C, 46.04; H, 4.48; S, 24.40.

1,4-Dithiane-2,6-dione (14).

Compound 14 was distilled as a pale yellow oil, bp 98° (3.0 torr); ¹H nmr: δ 3.67 (s, 4H, H-3, 5); ¹³C nmr: δ 40.2 (C-3, 5), 192.6 (C-2, 6).

Anal. Calcd. for $C_4H_4S_2O_2$: C, 32.41; H, 2.72; S, 43.27. Found: C, 32.34; H, 2.67; S, 43.11.

4-Oxathiane-2,6-dione (15).

The crude thioanhydride was distilled as a colorless oil, bp 110° (3.0 torr); 1H nmr: δ 4.35 (s, 4H, H-3, 5); ^{13}C nmr: δ 73.0 (C-3, 5), 193.8 (C-2, 6).

Anal. Calcd. for $C_4H_4SO_3$: C, 36.37; H, 3.05; S, 24.22. Found: C, 36.52; H, 3.45; S, 24.40.

3-Phenylthiane-2,6-dione (16).

The crude thioanhydride was obtained as pale yellow solid, which was recrystallized (methylene chloride-pentane) to afford white crystalline solid, mp $69-70^\circ$; 1H nmr: δ 2.44 (cm, 2H, H-4_{a,b}), 2.85 (ddd, 1H, J = 5.7, 8.6, 17.6, H-5_a), 2.98 (ddd, 1H, J = 4.3, 5.9, 17.6, H-5_b), 3.92 (dd, 1H, J = 5.0, 8.7, H-3), 7.17-7.40 (cm, 5H, Ph); ^{13}C nmr: δ 26.3 (C-4), 39.6 (C-5), 55.6 (C-3), 127.5, 127.7, 128.5, 136.7 (Ph), 197.3 (C-6), 197.8 (C-2).

Anal. Calcd. for $C_{11}H_{10}SO_2$: C, 64.05; H, 4.88; S, 15.54. Found: C, 63.99; H, 4.76; S, 15.31.

3,3-Dimethylthiane-2,6-dione (17).

The crude thioanhydride was distilled as a colorless oil, bp 121° ; 1H nmr: δ 1.33 (s, 6H, CH_3), 1.98 (cm, 2H, H-4), 2.86 (cm, 2H, H-5); ^{13}C nmr: δ 24.4 (CH_3), 32.7 (C-4), 37.1 (C-5), 45.0 (C-3), 198.3 (C-6), 202.3 (C-2).

Anal. Calcd. for $C_7H_{10}SO_2$: C, 53.15; H, 6.38; S, 20.23. Found: C, 53.43; H, 6.35; S, 20.16.

8-Thiaspiro[4,5]decane-7,9-dione (18).

Compound **18** distilled as a colorless oil, bp 148° (3.0 torr); 1H nmr: δ 1.61 (cm, 4H, H-2, 3), 1.71 (cm, 4H, H-1, 4), 2.77 (s, 4H, H-6, 10); ^{13}C nmr: δ 23.9 (C-2, 3), 37.5 (C-1, 4), 40.7 (C-5), 52.2 (C-6, 10), 197.1 (C-7, 9).

Anal. Calcd. for $C_9H_{12}SO_2$: C, 58.68; H, 6.57; S, 17.37. Found: C, 58.84; H, 6.54; S, 16.99.

Dibenzthiepane-2,7-dione (Diphenic Thioanhydride) (19).

Method A.

To a solution of sodium sulfide (10 mmoles) in water/THF (50/50 ml) was added 10 mmoles of diphenic anhydride and stirred for 10 minutes. To this solution, additional diphenic anhydride (10 mmoles) was added and the reaction mixture stirred for 30 minutes. Washing with sodium bicarbonate was omitted during workup. The crude product was triturated with hot pentane (8 x 25 ml) and the solvent evaporated to give a white solid, mp $85-86^\circ$ (lit $91-92^\circ$); 1H nmr: δ 7.35-7.71 (cm, 8H, Ph); ^{13}C nmr: δ 126.8, 128.6, 131.5, 132.4, 134.9, 139.8 (Ph), 190.8 (C-2, 7) [21].

Anal. Calcd. for $C_{14}H_8SO_2$: C, 69.98; H, 3.35; S, 13.34. Found: C, 69.76; H, 3.54; S, 12.99.

4,5-Benzothiepane-2,7-dione (20).

The crude thioanhydride was recrystallized from methylene chloride-pentane to afford pale yellow needles, mp $106-107^\circ$; 1H nmr: δ 4.29 (s, 4H, H-3, 6), 7.33 (cm, 4H, Ph); ^{13}C nmr: δ 51.6 (C-3, 6), 128.67, 129.9, 130.2 (Ph), 193.7 (C-2, 7).

Anal. Calcd. for $C_{10}H_8SO_2$: C, 62.48; H, 4.19; S, 16.67. Found: C, 62.26; H, 4.12; S, 16.37.

trans-Bicyclo[5.4.0^{1,7}]thiaundecane-3,5-dione (21).

The diacid was synthesized by a literature procedure [27,28]. The crude thioanhydride was distilled to afford a colorless oil, bp 156° (3.0 torr), which crystallized to a white solid; 1H nmr: δ 1.29 (cm*, 4H), 1.76 (cm*, 6H), 2.76 (cm*, 2H, J = 5.8, 15.5 Hz, H-2_a, 6_a), 3.02 (cm*, 2H, J = 3.8, 15.5 Hz, H-2_b, 6_b), *High order; ^{13}C nmr: δ 25.6 (C-9, 10), 32.6 (C-8, 11), 39.9 (C-1, 7), 51.5 (C-2, 6), 197.5 (C-3, 5).

Anal. Calcd. for $C_{10}H_{14}SO_2$: C, 60.57; H, 7.11; S, 16.17. Found: C, 60.60; H, 7.43; S, 16.42.

5-Thiaspiro[2,3]hexane-4,6-dione (22).

The crude product was obtained as white needles from pentane at -78° , (pale yellow oil at 20°), bp 46° (3.1 torr); 1H nmr: δ 1.92 (s, 4H); ^{13}C nmr: δ 20.4 (C-1, 2), 58.6 (C-3), 188.7 (C-4, 6).

Anal. Calcd. for $C_5H_4SO_2$: C, 46.88; H, 3.15; S, 24.98. Found: C, 46.59; H, 3.41; S, 24.81.

2-Thiaspiro[3,3]heptane-4,6-dione (23).

The crude product crystallized as white needles from pentane at -78° , (pale yellow oil at 20°); 1H nmr: δ 1.95 (cm, 2H), 2.68 (cm, 4H); ^{13}C nmr: δ 14.9 (C-6), 29.6 (C-5, 7), 90.5 (C-3), 187.0 (C-2, 4). Physical and pmr data are in agreement with literature values [11,12].

3,3-Dimethylthietane-2,4-dione (24).

The crude product was crystallized as white needles from pentane at -78° , (colorless oil at 20°); 1H nmr: δ 1.52 (s, 6H); ^{13}C nmr: δ 19.3 (CH_3), 90.8 (C-3), 188.9 (C-2, 4). Physical and pmr data are in agreement with literature values [11,12].

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