(39) R. F. Zurcher in "Progress in Nuclear Magnetic Resonance Spectroscopy," Vol. II, J. W. Emsley, J. Feeney, and L. H. Sutcliffe, Ed., Pergamon Press, New York, N. Y., 1967, Chapter 5, especially p 212.

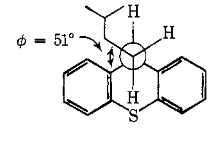
(40) For excellent reviews, see G. E. Bachers and T. Schaffer, *Chem. Revs.*, **71**, 617 (1971); J. H. Noggle and R. E. Schirmer, "The Nuclear Overhauser Effect," Academic Press, New York, N. Y., 1971; R. A. Bell and J. K. Saunders, *Topics Stereochem.*, **7**, 1 (1973).

(41) NOE values represent the average of ~8–10 determinations and are considered reproducible to ±5% of the given value.

(42) Confirmation of these values was obtained by irradiating the methyl resonance (δ 0.79 ppm) of the ethyl group causing the complex methylene region to collapse to an eight-line spectrum. The four-line, low field segment was consistent with a vicinal coupling of 6.2 Hz while the more shielded component gave 9.0 Hz.

(43) M. Karplus, *J. Amer. Chem. Soc.*, **85**, 2870 (1963), and references therein.

(44) The results of an X-ray study on 9-isobutyl-T indicate that in the solid state the isobutyl group is in the pseudo-axial conformation and describes a torsional angle about the thioxanthene frame of 51°. See S. C. Chu, *Acta Crystallogr.*, **B29**, 1690 (1973), and S. S. C. Chu and B. Chung, *ibid.*, **B29**, 2253 (1973), and references contained therein.



(45) It is recognized that other factors may also contribute to these changes in relative chemical shifts (*vide supra*).

(46) All melting points were obtained in a Mel-Temp apparatus (open capillary) and are corrected. Pmr spectra were recorded on Varian Models HA-100 and A-60 nmr spectrometers in deuteriochloroform unless otherwise indicated. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn., and Crobaugh Laboratories, Cleveland, Ohio. All compounds were shown to be a homogeneous by thin layer chromatography (silica gel substrate) on glass plates using ethyl acetate or chloroform as eluents and with uv and iodine vapor for visualization. Mass spectra were obtained on a Varian Model M-66 mass spectrometer. Ir spectra were recorded using a Beckman Model IR-8 spectrophotometer. All alkylation reactions were carried out in a nitrogen atmosphere.

(47) On standing this material eventually solidified to produce an off-white solid, mp 42–43°.

(48) C. C. Price, M. Hori, T. Parasaran, and M. Polk, *J. Amer. Chem. Soc.*, **85**, 2278 (1963).

(49) 3 ft × ¼ in. aluminum column, 20% SE-30 on Aeropak.

(50) Thoxanthene is presumed to arise *via* a hydride transfer reaction from *tert*-butyllithium to the thioxanthylium ion. Attempted preparations of **7** by the direct alkylation of the thioxanthyl anion with *tert*-butyl halides have been unsuccessful thus far.

(51) E. G. Marsden and S. Smiles, *J. Chem. Soc.*, 1353 (1911).

(52) The reaction is similar to that already described[14] for the reduction of 1-methyl-4-chlorothioxanthone to 1-methyl-4-chlorothioxanthene.

Syntheses of Cyclic Bisthioacylals. 1,3-Dithiane-4,6-diones and 1,3-Dithiolane-4,5-dione[1]

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Reaction of bisthiomalonic acids **1a,b** with isopropenyl acetate gave thietanediones **3a,b** and thioacetone *via* Grob fragmentation (Scheme I, path a). When bisthio acid **1a** was treated with carbonyl compounds (acetone, acetaldehyde, acetophenone, and benzophenone) and boron trifluoride etherate, **3a** was again obtained (path a) except in the case of *p*-anisaldehyde, where path b was competitive and the 1,3-dithiane-4,6-dione **4c** was also obtained. Treatment of the pyridinium salt of **1a** with methylene iodide or dichlorodiphenylmethane also gave **3a**. The title compounds (**7a, 8c,d,f–i**) were alternately prepared by condensation of oxalyl, malonyl, and certain substituted malonyl halides with *gem*-dithiols. Selective methylation of compounds **8d**, **8e**, and **8g** at C-2 and/or C-5 was achieved.

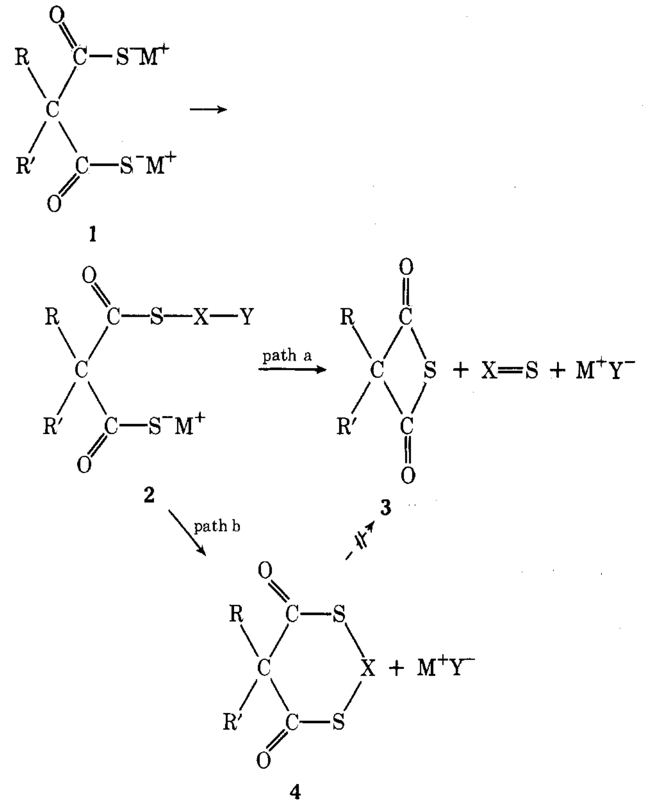
Although 1,3-dioxane-4,6-diones such as Meldrum's acid (**8a**) and a number of its derivatives have received considerable attention,[2] the 1,3-dithio analogs have not been studied. Herein we report the results of investigations into synthetic approaches to these sulfur heterocycles.

Reaction of dimethylmalonic acid with isopropenyl acetate catalyzed by sulfuric acid is known to give 2,2,5,5-tetramethyl-1,3-dioxane-4,6-dione (**8b**).[2a] In contrast, we have observed that reaction of dimethylbisthiomalonic acid (**1a**) or cyclobutane-1,1-bisthiodicarboxylic acid (**1b**) with isopropenyl acetate under similar conditions afforded the thietanes **3a** and **3b**, respectively, plus thioacetone. This apparently occurs *via* Grob fragmentation[3,4] of the expected intermediates **2a** and **2b** (Scheme I, path a) rather than ring closure to the 1,3-dithiane-4,6-diones (**4a, 4b**, path b). The latter compounds have been synthesized alternately (*vide infra*) and are stable both thermally and toward sulfuric acid, thus excluding them as intermediates to the thietanediones. The possibility that the thietanediones **3a** and **3b** might form directly by acid-catalyzed loss of hydrogen sulfide from the bisthio acids was also ruled out. Thus, the bisthio acids **1a** and **1b** underwent only slow loss of carbonyl sulfide in the presence of sulfuric acid.

Reaction of dimethylbisthiomalonic acid with *p*-anisaldehyde and boron trifluoride etherate in refluxing methylene chloride solution[5] again provided the thietanedione **3a**; however, it was accompanied by 2-(*p*-anisyl)-5,5-dimethyl-1,3-dithiane-4,6-dione (**4c**) in 26% yield. In this case reaction *via* **2c** (Scheme I, path b) apparently competes with Grob fragmentation (path a) and both products are observed. Since **4c** was thermally stable at its melting point (119–124°) it was considered an unlikely precursor to the thietanedione.

Formation of the bisthioacylal **4c** from dimethylbisthiomalonic acid and anisaldehyde–boron trifluoride prompted us to examine such reactions with other carbonyl compounds. Reaction of the bisthio acid with benzophenone or acetone and boron trifluoride gave only thietanedione accompanied by thiobenzophenone or thioacetone, respectively. Similar reactions with acetophenone and with acetaldehyde also netted some thietanedione **3a** (glpc, nmr) but again none of the bisthioacylals (**4f, 4g**). When

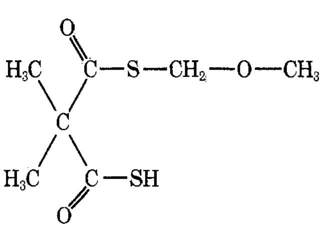
Scheme I



R = R′ = CH_3, except for **1b**–**4b** for which R, R′ = $(CH_2)_3$

	M^+	X	Y
a	H^+	$C(CH_3)_2$	OAc
b	H^+	$C(CH_3)_2$	OAc
c	H^+	$CH(p\text{-}C_6H_4OCH_3)$	OBF_3^-
d	H^+	CPh_2	OBF_3^-
e	H^+	$C(CH_3)_2$	OBF_3^-
f	H^+	CCH_3Ph	OBF_3^-
g	H^+	$CHCH_3$	OBF_3^-
h	H^+	CH_2	$OCH_3BF_3^-$
i	PyH^+	CH_2	I
j	PyH^+	CPh_2	Cl

methylal–boron trifluoride was employed as the electrophilic reagent, **3a** was accompanied by an isolable, unstable compound which was assigned structure **5** on the basis of ir and nmr spectral data. This structure, of course, represents the uncomplexed form of intermediate **2h**.

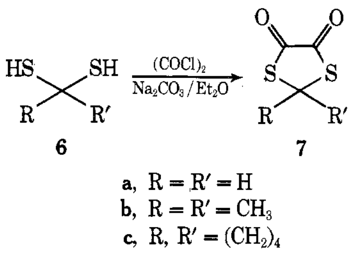


5

The unique formation of bisthioacylal **4c** from the anisaldehyde–boron trifluoride reaction was quite striking. It appears likely that competitive formation of **4c** may result from a fortuitous combination of enhanced carbonium ion stabilization coupled with a sufficiently low steric factor to permit ring closure *via* path b, Scheme I.

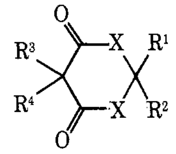
An attempt to prepare 5,5-dimethyl-1,3-dithiane-4,6-dione (**4i**) by reaction of the pyridinium salt of dimethylbisthiomalonic acid with methylene iodide yielded thietanedione **3**, presumably by loss of thioformaldehyde[6] and iodide ion. Likewise, reaction of the pyridinium salt of the bisthio acid with dichlorodiphenylmethane netted thietanedione and thiobenzophenone.[7] These reactions are also explained *via* path a, Scheme I (intermediates **2i, 2j**).

Although 1,3-dithiane-4,6-diones were not generally accessible *via* the bisthiomalonic acids, these compounds have been synthesized alternately. In 1962, Jentzsch, Fabian, and Meyer reported the synthesis of three 1,3-dithiolane-4,5-diones (**7b–d**) by condensation of the *gem*-dithiols **6b–d** with oxalyl chloride.[8] We have further investigated this reaction with the hope of extending it to the synthesis of other five- to seven-membered ring bisthioacylals. Although it appears to be of rather limited scope, we have utilized it for preparation of the parent, 1,3-dithiolane-4,5-dione (**7a**), and certain 1,3-dithiane-4,6-diones (**8c,d,f–i**).



6 **7**

a, R = R′ = H
b, R = R′ = CH_3
c, R, R′ = $(CH_2)_4$
d, R, R′ = $(CH_2)_5$



8

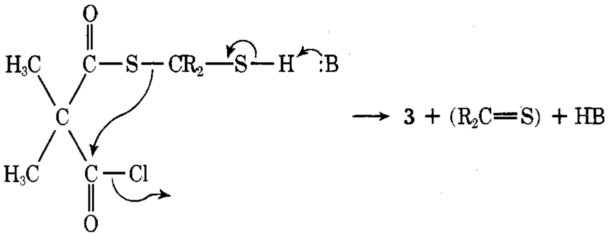
Compd	X	R^1	R^2	R^3	R^4
a	O	CH_3	CH_3	H	H
b	O	CH_3	CH_3	CH_3	CH_3
c	S	H	H	H	H
d	S	H	H	CH_3	H
e	S	CH_3	H	H	H
f	S	CH_3	CH_3	H	H
g	S	CH_3	CH_3	CH_3	H
h	S	H	H	$CH_2CH_2CH_2$	
i	S	$CH_2CH_2CH_2$		$CH_2CH_2CH_2$	
j	S	CH_3	CH_3	=CHPh	
k	S	CH_3	CH_3	$=CH(p\text{-}C_6H_4NO_2)$	

1,3-Dithiolane-4,5-dione (**7a**) was obtained by reaction of oxalyl bromide with methanedithiol and pyridine in ether solution. Use of pyridine rather than anhydrous sodium carbonate resulted in a marked acceleration of the reaction rate and avoided side reactions due to hydrogen bromide (which was not effectively removed by sodium carbonate).

Reaction of malonyl chloride with methanedithiol in chloroform (room temperature) resulted in evolution of hydrogen chloride which continued for ~1.5 hr. Work-up at that time provided 1,3-dithiane-4,6-dione (**8c**) in 53% yield; however, when the reaction was continued for several hours longer, only intractable material could be isolated. Addition of either pyridine or sodium carbonate to the reaction mixture caused a decrease to <5% in yield.

Reaction of methyl- or dimethylmalonyl chloride or cyclobutane-1,1-dicarboxylic acid chloride with methanedithiol in chloroform did not provide the 5-substituted 1,3-dithiane-4,6-diones (**8d, 4h, 8h**); however, **8d** and **8h** were obtained in 19 and 51% yields, respectively, when the reactions were carried out in the presence of 2 equiv of pyridine.

Examination of the crude products from reaction of dimethylmalonyl chloride with methanedithiol in the absence of pyridine revealed the formation of dimethylthietanedione **3** in low yield, presumably *via* Grob fragmentation of intermediate **9a** with loss of thioformaldehyde and hydrogen chloride.

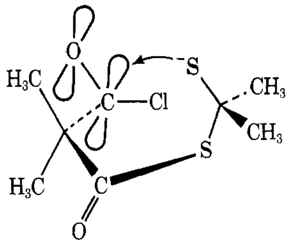


9

a, R = H; B = Cl^-
b, R = CH_3; B = pyridine

2,2-Dimethyl-1,3-dithiane-4,6-dione (**8f**) and its 5-methyl derivative **8g** have been obtained in 50 and 37% yields by reaction of malonyl chloride or methylmalonyl chloride, respectively, with propane-2,2-dithiol and sodium carbonate in ether solution. These products were accompanied by 2,2,4,4,6,6-hexamethyl-1,3,5-trithiane, which results from hydrogen chloride catalyzed reaction of propane-2,2-dithiol. Attempts to carry out these reactions in the presence of pyridine resulted in intractable products.

2,2,5,5-Tetramethyl-1,3-dithiane-4,6-dione (**4a**) was not accessible by reaction of dimethylmalonyl chloride and propane-2,2-dithiol with sodium carbonate in ether solution. When pyridine was employed as the base, dimethylthietanedione (**3**) was again identified, apparently *via* Grob fragmentation of intermediate **9b**. It is to be expected that attack of the SH or Ssupn− group of propane-2,2-dithiol on the carbonyl group of dimethylmalonyl chloride would be sterically hindered owing to methyl–methyl and methyl–sulfur interactions, especially during ring closure, depicted in structure **10**. Cyclobutane-1,1-dicarboxylic acid chloride was expected to exhibit a smaller steric effect than dimethylmalonyl chloride; however, reaction of the cyclobutane-1,1-dicarboxylic acid chloride with propane-2,2-dithiol in the absence or presence of pyridine failed to provide the 1,3-dithiane-4,6-dione (**4b**). Interestingly, when the steric requirement of the dithiol moiety was also decreased by use of cyclobutane-1,1-dithiol, the 1,3-dithiane-4,6-dione **8i** was obtained in 39% yield.



10

By analogy to the unusual acidity exhibited by Meldrum's "acid" (**8a**),[2a] the 1,3-dithiane-4,6-diones **8c,d** and **8e–g** possessing hydrogen at the 5 position are soluble in 5% sodium bicarbonate solution.

The potassium enolate of 2,2-dimethyl-1,3-dithiane-4,6-dione (from **8f** and potassium hydride in DMF) underwent methylation to provide **8g** in very low yield; however, the enolates derived from **8d** and **8g** with sodium hydride in DMF proved to be more reactive, yielding **4h** and **4a** in yields of 63 and 42%, respectively.

It was anticipated that the dianion resulting from deprotonation of the 1,3-dithiane-4,6-dione system at C-2 and C-5 could be utilized to effect selective alkylation at the 2 position. Treatment of **8c** with 2 mol of *tert*-butyllithium or *n*-butyllithium in THF solution, followed by methylation with methyl iodide, did afford the 2-methyl compound **8e**, albeit only in very low yield. Although a large amount of starting material was recovered, 5-methylated products were not observed.

Shuster, *et al.*, condensed Meldrum's acid (**8a**) with various substituted benzaldehydes using Knoevenagel conditions.[9] In a similar manner the 1,3-dithiane-4,6-dione **8f** condensed with benzaldehyde to yield the benzylidene derivative fb8j in 11% yield. *p*-Nitrobenzaldehyde yielded none of the benzylidene derivative **8k**.

Experimental Section

General. Spectral, microanalytical, and yield data and melting points and/or boiling points for new compounds are listed in Table I.

Nmr spectra were recorded with a Varian Associates A-60 spectrometer on $CDCl_3$ and benzene-d_6 solutions. Chemical shifts are reported in δ units (parts per million) downfield from internal tetramethylsilane. Ir spectra were obtained on KBr disks (unless noted otherwise in Table I) with a Perkin-Elmer Model 337 grating spectrophotometer. Glpc was carried out on a Hewlett-Packard F & M Model 700 instrument, employing a 6 ft × 0.25 in. stainless steel column packed with 10% SE-30 on silanized 60–80 mesh Chromosorb W. Tlc was performed on Quantum Industries Q1F plates. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Melting points and boiling points are uncorrected.

Oxalyl bromide and malonyl chloride (Aldrich Chemical Co.), 98% boron trifluoride etherate (Matheson Coleman and Bell), *n*-butyllithium (Foote Mineral Co.), and potassium hydride and sodium hydride (Ventron Corp.) were used as received. Methanedithiol (**6a**),[10,11] propane-2,2-dithiol (**6b**),[8] cyclobutane-1,1-dithiol,[12] methylmalonyl chloride,[13] dimethylmalonyl chloride,[14] cyclobutane-1,1-dicarboxylic acid chloride,[15] dimethylbisthiomalonic acid (**1a**),[16] and cyclobutane-1,1-bisthiodicarboxylic acid (**1b**)[16] were prepared according to literature procedures.

Reaction of Dimethylbisthiomalonic Acid (1a) and Cyclobutane-1,1-bisthiodicarboxylic Acid (1b) with Isopropenyl Acetate. To 10 mmol of **1a** or **1b** in 10 mmol of isopropenyl acetate was added dropwise, with stirring, 0.1 ml of concentrated H_2SO_4. After stirring at room temperature for 24 hr the reaction mixture was distilled. In the case of **1b**, 0.79 g (56%) of 3,3-trimethylenethietanedione (**3b**), bp 40° (0.5 mm), was obtained, accompanied by the characteristic vile odor of thioacetone. When **1a** was employed, 0.65 g (50%) of 3,3-dimethylthietanedione (**3a**), bp 85° (16 mm), was obtained, also accompanied by the stench of thioacetone. The thietanediones **3a** and **3b** were identified by comparison of their ir and nmr spectra and glpc retention times with those for authentic samples.[16]

Stability of 1a to Sulfuric Acid or Boron Trifluoride Etherate. To 0.5 ml of a saturated solution of concentrated H_2SO_4 in benzene-d_6 in an nmr tube was added 50 mg of pure **1a**. No changes were observed in the nmr spectra obtained on this sample over a 15-hr period.

An 82-mg sample of **1a** and an equimolar amount of boron trifluoride etherate in 0.25 ml of CH_2Cl_2 in an nmr tube was heated at 62° for 2 hr. The solvent was removed. Nmr (benzene-d_6) showed only **1a** and a trace of thietane-2,4-dione (**3a**).

2-(*p*-Anisyl)-5,5-dimethyl-1,3-dithiane-4,6-dione (4c). Anisaldehyde (272 mg, 2.0 mmol) and **1a** (352 mg, 2.0 mmol) were combined, under nitrogen, in 10 ml of methylene chloride. The mixture was refluxed for 2 hr, cooled to room temperature, washed with two 30-ml portions of 2% Na_2CO_3 solution, dried ($MgSO_4$), and filtered. The filtrate was evaporated to yield a red oil which crystallized. Sublimation of the crude product at 135° (0.05 mm) gave 148 mg of **4c**. Recrystallization from cyclohexane or resublimation yielded analytically pure **4c**.

Analysis of the crude reaction mixture by glpc and nmr indicated the presence of **3a**.

Reaction of 1a with Acetaldehyde, Acetone, Acetophenone, and Benzophenone in the Presence of Boron Trifluoride Etherate. Five millimoles each of **1a** and the corresponding carbonyl compound were combined, under nitrogen, in 20 ml of methylene chloride. The mixtures were heated under reflux in an oil bath at 60° and 0.4 ml of boron trifluoride etherate was added. After 24 hr the reaction mixtures were analyzed by glpc, tlc, and nmr. In all

Table I
Physical Data

Compd[a]	Mp, °C	Bp, °C (mm)	Yield, %	Ir,[b] cm^{-1}	Nmr, δ
4a	49–56	122–128 (2.8)	42	1658, 1681[c]	1.60 (s, 6, C-5 CH_3's), 1.97 (s, 6, C-2 CH_3's)
4c	119–124		26	1645, 1675	1.48 (s, 3, C-5 CH_3), 1.70 (s, 3, C-5 CH_3), 3.80 (s, 3, OCH_3) 6.25 (s, 1, H), 7.19 (AA'BB' pattern, 4, aromatic)
4h	53–56		63	1653, 1672	1.55 (s, 6), 4.51 (s, 2)
7a	91–93		38	1658	4.64 (s, 2)
8c	101–104		53	1661	4.07 (s, 2, C-5 H's), 4.59 (s, 2, C-2 H's)
8d	101–106	125–140 (0.4–1.0)	19	1667, 1692	1.35 (d, 3, J = 6.5 Hz), 4.29 (q, 1, J = 6.5 Hz), 4.20, 4.98 (AB, d of d, J = 15.0 Hz)[d]
8e	59–62		6	1669	1.80 (d, 3, J = 7.0 Hz), 3.79, 4.07 (AB, d of d, J = 14.5 Hz), 5.35 (q, 1, J = 7.0 Hz)
8f	88–89	144 (0.1)	50	1658	2.02 (s, 6), 4.01 (s, 2)
8g	85–86		37	1664, 1692	1.44 (d, 3, J = 6.5 Hz), 1.88 (s, 3), 2.18 (s, 3), 4.17 (q, 1, J = 6.5 Hz)
8h	87–89	118–138 (0.4–0.35)	51	1653	2.04 ("quintet," 2, J = 8.0 Hz), 2.89 ("t," 4, J = 8.0 Hz), 4.37 (s, 2)
8i	131.5–134.5		39	1667	2.27 (m, 4), 2.80 (m, 8)
8j	135–141		11	1667, 1647	2.00 (s, 6), 7.60 (s, 1),[e] 7.28–7.78 (m, 5)
5		83–89 (0.4–0.35)	23	1672, 1698, 1736	1.55 (s, 6), 3.35 (s, 3), 5.12 (s, 2), 6.15 (s, 1)

[a] Satisfactory analytical data (±0.35% for C, H, S) were obtained for all compounds, except **5**, listed in this table. [b] All of the compounds listed exhibited rather complex bands in the C=O stretch region. This phenomenon has also been observed with Meldrum's acid (**8a**) and is ascribed to vibrational coupling (ref 17). [c] Liquid film. [d] CD_2Cl_2 solution. [e] The chemical shift of the benzylidene proton was verified by use of Ventron's Eu-Resolve-II.

cases **3a** was identified by nmr and by glpc using the retention time and the technique of peak potentiation with an authentic sample.[16] The 1,3-dithiane-4,6-diones could not be detected by nmr. Also, in the case of acetone, tlc comparison of the reaction mixture with authentic **4a** prepared by an alternate route (*vide infra*) failed to indicate this product.

In the case of benzophenone, careful distillation of the reaction mixture yielded 0.38 g (58%) of **3a** and 0.67 g (68%) of the intensely blue thiobenzophenone, bp 111–114° (0.4 mm) [lit.[18] bp 174° (14 mm)]. The other reaction mixtures did not yield isolable products.

Reaction of 1a with Methylal and Boron Trifluoride Etherate. Methylal (380 mg, 5 mmol) and **1a** (821 mg, 5 mmol) were combined, under nitrogen, in 20 ml of methylene chloride. The reaction mixture was heated under reflux in an oil bath at 60° and 0.4 ml of boron trifluoride etherate was added. The mixture was refluxed for 43 hr and then analysed by glpc, tlc, and nmr. **3a** was present in ~40% yield. Distillation of the reaction mixture gave 0.24 g of a liquid, bp 83–89° (0.4–0.35 mm), which gave nmr and ir spectra consistent with structure **5**.

Reaction of Diiodomethane with 1i. To a solution of pyridine (0.79 g, 10 mmol) and **1a** (0.82 g, 5 mmol) in 50 ml of anhydrous ether was added diiodomethane (1, 34 g, 5 mmol) over a period of 20 min. After stirring for 1 hr longer the pyridinium iodide was precipitated by the addition of chloroform and removed by filtration. The filtrate was carefully distilled through a Vigreux column to provide pure **3a** (nmr, glpc).

Reaction of Dichlorodiphenylmethane with 1j. To a solution of **1a** (3.29 g, 0.02 mol) and pyridine (3.16 g, 0.04 mol) in 50 ml of ice-cold chloroform was added dichlorodiphenylmethane (4.76 g, 0.02 mol). The mixture was stirred for 3 hr at 60° under nitrogen. The blue color of thiobenzophenone was apparent after a few minutes. After the chloroform was removed the crude product was distilled at 58° (14 mm) to give **3a** in ~80% yield accompanied by unidentified impurities (nmr). The ir spectrum of a sample of the distillation residue was very similar to that of authentic thiobenzophenone.[18]

1,3-Dithiolane-4,5-dione (7a). Oxalyl bromide (4.32 g, 0.02 mol) was added over a 3–5-min period to a solution of **6a** (1.80 g, 0.02 mol) and dry pyridine (3.16 g, 0.04 mol) in 40 ml of cold (ice bath) anhydrous ether. After stirring overnight at room temperature the mixture was filtered through Celite and the ether was evaporated to yield an off-white solid. Recrystallization from carbontetrachloride–chloroform gave 1.02 g of **7a** as white needles.

1,3-Dithiane-4,6-dione (8c). A solution of 2.82 g of malonyl chloride and 1.80 g of **6a** (0.02 mol of each) in 7 ml of chloroform was stirred at room temperature for 1.5 hr. The reaction mixture was poured into 70 ml of ice-cold 10% Na_2CO_3 solution. The chloroform layer was removed and discarded. The aqueous phase was cooled by addition of ice, acidified with 10% HCl, and extracted three times with 40-ml portions of methylene chloride. The combined extract was dried ($MgSO_4$) and evaporated to yield 1.55 g of crude orange crystals. Recrystallization from benzene–cyclohexane or sublimation at 65° (2.0 mm) yielded white crystals of **8c**.

1,3-Dithiane-4,6-diones (8d,h,i). To a solution of 0.02 mol of the appropriate *gem*-dithiol and 0.04 mol of pyridine in 40 ml of chloroform was added (ice-bath cooling) 0.02 mol of the appropriate acid chloride, over a period of 5 min. The reaction mixtures were stirred for 16 hr at room temperature, 4 hr under reflux, and 12 hr under reflux, respectively, for **8d, 8h,** and **8i**. The chloroform was then removed on a rotary evaporator to obtain a solid residue which was triturated with three portions of boiling ether. The ether solution was filtered through Celite and evaporated to yield the crude product.

The crude **8i** was triturated with boiling petroleum ether (bp 30–60°) and filtered to collect 1.84 g of crude product. Recrystallization from cyclohexane yielded an analytical sample. Crude **8d** and **8h** were purified by short-path distillation *in vacuo*. The distillates, which crystallized upon cooling, were recrystallized: **8d,** 0.62 g, from benzene–cyclohexane; **8h,** 1.92 g, from cyclohexane.

5,5-Dimethyl-1,3-dithiane-4,6-dione (4h). To a cold (ice bath) stirred solution of **8d** (533 mg, 3.29 mmol) in 2 ml of dry dimethylformamide (DMF), under nitrogen, was added 153 mg of a 57% oil dispersion of sodium hydride (3.62 mmol). The mixture was stirred for 15 min, and then methyl iodide (560 mg, 3.95 mmol) was added. After stirring for 16 hr longer at room temperature, the mixture was poured into 50 ml of ice water and extracted four times with 20-ml portions of methylene chloride. The combined extract was washed twice with 30-ml portions of cold 10% Na_2CO_3 solution, dried ($MgSO_4$), and evaporated to a residue which was extracted once with boiling petroleum ether (30–60°) to remove the mineral oil. After evacuation at 40° (0.1 mm) to remove DMF, the crude **4h** (363 mg) was recrystallized from benzene–cyclohexane.

In an unsuccessful attempt to obtain **4h,** dimethylmalonyl chloride (3.38 g, 0.02 mol) and **6a** (1.80 g, 0.02 mol) were combined in 10 ml of chloroform and stirred for 27 days at room temperature. The solvent was then removed on a rotary evaporator and the crude product was distilled. 3,3-Dimethylthietane-2,4-dione (**3a**) was identified in the first fraction, bp 25–60° (14–15 mm), using the technique of peak potentiation with an authentic sample[16] by both glpc and nmr.

2-Methyl-1,3-dithiane-4,6-dione (8e). A solution of **8c** (1.44 g, 9.72 mmol) in 30 ml of tetrahydrofuran (THF) was prepared under nitrogen with Dry Ice–acetone bath cooling. To this solution was added, dropwise with stirring, 14.9 ml of a 13.01% solution of *n*-butyllithium in hexane (20.0 mmol). The mixture was stirred for 1 hr, and then 1.45 g (10.2 mmol) of methyl iodide was added. After 2 hr, 10 ml of dry THF was added and the mixture was allowed to stand at 5° for 5.5 days. Then 25 ml of 10% HCl was added and the mixture was extracted once with 20 ml of ether and twice with 30-ml portions of methylene chloride. The combined ether–methylene chloride extract was dried ($MgSO_4$) and evaporated to give 1.92 g of material. Column chromatography on silica gel (Woelm) with chloroform as the eluent, followed by tlc on an Analtech silica gel GF Uniplate (chloroform), provided 100 mg of **8e** which was 95% pure by glpc. Analytical samples were collected by glpc.

The use of *tert-*butyllithium under similar conditions also provided **8e;** however, the yield was <5% (nmr).

2,2-Dimethyl-1,3-dithiane-4,6-dione (8f). Anhydrous Na_2CO_3 (6.30 g, 0.06 mol) and **6b** (3.24 g, 0.03 mol) were placed in 100 ml of cold (ice bath) anhydrous ether under nitrogen. A solution of malonyl chloride (4.23 g, 0.03 mol) in 15 ml of ether was added, dropwise with stirring, over a period of 15 min. The mixture was stirred for 2 hr at the ice-bath temperature, then for 16 hr at room temperature. It was then filtered, and the filtrate was evaporated to remove the ether and then distilled *in vacuo.* After a forerun of 0.60 g of 2,2,4,4,6,6-hexamethyl-1,3,5-trithiane, 2.65 g of crude **8f,** bp 144° (0.1 mm), was obtained (crystallized upon cooling). The crude **8f** was recrystallized from cyclohexane.

Hexamethyl-1,3,5-trithiane results *via* acid-catalyzed reaction of the dithiol. Some HCl was present even in the presence of Na_2CO_3; however, when the carbonate was omitted, the yield of **8f** dropped from 50 to 19%. Hexamethyltrithiane of 95% purity [nmr δ 1.78 (s)] was prepared by stirring a solution of **6b** in chloroform saturated with HCl gas for 1 day at room temperature.[19]

2,2,5-Trimethyl-1,3-dithiane-4,6-dione (8g). Preparation of **8g** was carried out by reaction of methylmalonyl chloride and **6b** (0.04 mol each) with Na_2CO_3 in anhydrous ether by a procedure similar to that described for the preparation of **8f,** except that the reaction time was extended to 68 hr at room temperature. After filtration and evaporation of the ether, the crude product was dissolved in 50 ml of boiling cyclohexane, treated with Darco, and filtered. On cooling to room temperature, 2.25 g of white, crystalline **8g** was obtained (second crop 0.58 g). Recrystallization from cyclohexane provided analytically pure **8g.**

2,2,5,5-Tetramethyl-1,3-dithiane-4,6-dione (4a). Powdered sodium hydride (148 mg, 6.0 mmol, prepared from 260 mg of 57% oil dispersion) was added in several portions over a 10-min period to an ice-cold, stirred solution of **8g** (950 mg, 5.0 mmol) in 5 ml of dry DMF under nitrogen. After stirring for 10 min longer, methyl iodide (1.42 g, 10 mmol) was added, and then the mixture was stirred for 50 hr at room temperature and then poured into 75 ml of ice water. The mixture was extracted twice with 50-ml portions of ether. The combined extract was then washed three times with 100-ml portions of cold water, followed by two 100-ml portions of cold 2% HCl solution, dried ($MgSO_4$), and evaporated on the steam bath to yield 0.43 g of crude **4a.** The crude product was distilled *in vacuo.* The distillate crystallized very slowly upon standing at room temperature.

2,2-Dimethyl-5-benzylidene-1,3-dithiane-4,6-dione (8j). Benzaldehyde (1.59 g, 15 mmol), **8f** (1.76 g, 10 mmol), glacial acetic acid (0.18 ml), and dry piperidine (0.06 ml) were combined in 30 ml of dry benzene. The mixture was refluxed for 21.5 hr under a Dean-Stark trap and then washed in succession with three 30-ml portions of saturated $NaHSO_3$ solution, one 25-ml portion of 2% HCl, and one 30-ml portion of 10% Na_2CO_3 solution. The solution was dried ($MgSO_4$), filtered, and treated with Norit, and the solvent was evaporated to yield a red oil which partially crystallized on standing. This residue was triturated with anhydrous ether and filtered to collect 285 mg of yellow crystals of **8j.** Repeated sublimation, 150° (0.05 mm), provided analytically pure material.

Registry No.—**1a,** 34803-94-6; **1b,** 34803-96-8; **1i,** 52133-70-7; **3a,** 34804-00-7; **3b,** 34804-02-9; **4a,** 52133-71-8; **4c,** 52133-72-9; **4h,** 52133-73-0; **5,** 52133-74-1; **6a,** 6725-64-0; **6b,** 1687-47-4; **6** [R, R′ = $(CH_2)_3$], 15144-23-7; **7a,** 52133-75-2; **8c,** 52133-76-3; **8d,** 52133-77-4; **8e,** 52133-78-5; **8f,** 52133-79-6; **8g,** 52133-80-9; **8h,** 52133-81-0; **8i,** 52133-82-1; **8j,** 52133-83-2; malonyl chloride, 1663-67-8; methylmalonyl chloride, 39619-07-3; cyclobutane-1,1-dicarboxylic acid chloride, 51816-01-4; isopropenyl acetate, 108-22-5; anisaldehyde, 123-11-5; acetaldehyde, 75-07-0; acetone, 67-64-1; acetophenone, 98-86-2; benzophenone, 119-61-9; methylal, 109-87-5; diiodomethane, 75-11-6; dichlorodiphenylmethane, 2051-90-3; oxalyl bromide, 15219-34-8; dimethylmalonyl chloride, 5659-93-0; benzaldehyde, 100-52-7.

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