220-MHz nmr spectra were measured by the Physico-Chemical Measurements Unit, Harwell Didcot, Berkshire, England.

Registry No.—**1**, 5459-35-8; **2**, 920-37-6; **3a**, 51263-38-8; **3b**, 51263-39-9; **4**, 51263-40-2; **5**, 51263-41-3; **6**, 35143-10-3; **7**, 51263-42-4; **8a**, 51263-43-5; **8b**, 51263-44-6; **9**, 51263-45-7; **10a**, 51263-46-8; **11b**, 51263-47-9; **19a**, 35528-83-7; **19b**, 35528-84-8; *o*-mercaptophenol, 1121-24-0; ethyl 2,3-dibromobutanoate, 609-11-0; 1-methyl-3-chloro-5,6-dihydro-2(1*H*)-pyridone, 51263-48-0.

References and Notes

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(6) The higher isolated yield of **9** as compared with the mixture of **8a** and **8b**, although theoretically unexpected, probably resulted from the fact that **9** was isolated as a solid while the mixture of **8a** and **8b** was purified by distillation. As yet, attempts to separate **8a** and **8b** have been unsuccessful. Nmr of the reaction mixtures prior to purification failed to detect β-S-substituted reaction products.
(7) Although the α,β-unsaturated isomer is thermodynamically favored over the β,γ-unsaturated isomer, the ΔG° for the equilibrium is not large.
(8) The formation of unexpected products in the reaction of catechol with α-bromocrotonate esters has also been explained by these phenomena (see ref 1).
(9) We thank one of the reviewers for suggesting this intriguing possibility. Mechanistic studies are underway and will constitute the subject of a future report from our laboratory.
(10) G. Modena, *Accounts Chem. Res.*, **4**, 73 (1971).
(11) The failure to isolate **10b** and **11a** from the reaction mixture does not rule out their possible formation in small quantities (undetected by nmr).
(12) Similar double-bond migrations have been observed in 6-hydroxyhexenoic lactones [C. G. Overberger and H. Kaye, *J. Amer. Chem. Soc.*, **89**, 5640 (1967)] and in tetrahydro-2*H*-azepin-2-ones [H. K. Reimschuessel, J. P. Sibilia, and J. V. Pascale, *J. Org. Chem.*, **34**, 959 (1969)].
(13) The isolation, characterization, and Michael-type ring closure reactions of **15** and **18** will be subject of a future publication from this laboratory.

Synthesis of ω-1,3-Dithianyl Carboxylic Acids *via* Cleavage of Cyclic α-Diketone Monothioketals

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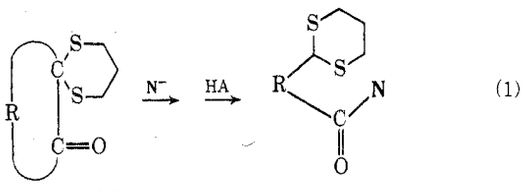
A number of cyclic (C_6–C_8) α-diketone monothioketals were prepared *via* hydroxymethylation of the parent monoketone followed by treatment with 1,3-propanedithiol ditosylate. Cleavage of these simple cyclic systems took place readily in KOH–*tert*-butyl alcohol to give, after acidification, ω-1,3-dithianyl carboxylic acids in 88–95% yield. The attempted cleavage of an α',α'-dimethylated cyclohexane-1,2-dione monothioketal with KOH–*tert*-butyl alcohol failed, apparently because of steric hindrance to carbonyl addition. A thioketal ketone derived from an α,β-unsaturated cyclohexanone likewise failed to cleave. In this case enolization took place leading to the β,γ-unsaturated ketone derivative. Methanolic sodium methoxide or methanolic potassium hydroxide were ineffective in the cleavage reaction. These findings are consistent with a mechanism involving hydroxide addition to the carbonyl followed by proton abstraction by *tert*-butoxide leading to a reactive dialkoxy anion which undergoes C–C bond cleavage.

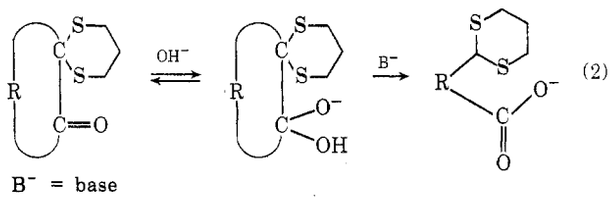
In a preliminary report we described the apparent nucleophilic cleavage of α-diketone monothioketals to give ω-dithianyl carboxylic acid derivatives (eq 1).[1] Subse-



(1)

N = nucleophile

quent studies indicated that the above cleavage reaction most likely proceeds in two stages with initial attack by hydroxide on the carbonyl followed by subsequent proton abstraction of the presumed adduct (eq 2).[2] The essential



(2)

B⁻ = base

features of eq 2 had previously been proposed by Gassman in connection with his studies on the Haller–Bauer-type cleavage of nonenolizable ketones.[3] Employing his reaction conditions (NaOH, NaO-*t*-Bu, *t*-BuOH, ether) we succeeded in obtaining ω-dithianyl carboxylic acids from certain unhindered decalones in over 90% yield.[2] We have now completed more definitive studies on this cleavage reaction which shed light on its scope and synthetic potential.

As noted above, Gassman's work and our own experience[2] indicated that a combination of hydroxide plus a strong (alkoxide) base afforded the highest yields of cleavage products. In an effort to simplify the experimental procedure we investigated the use of powdered potassium hydroxide in *tert*-butyl alcohol, a base system previously employed by Meyers, *et al.*[4] As shown below (Chart I), under appropriate conditions excellent results could be obtained using this base system with various cyclic α-diketone monothioketals. Optimum yields were realized when the temperature was maintained near 60°. Higher temperatures led to colored decomposition products and lower temperatures prolonged the required reaction times.

In contrast to the results obtained with decalone **9** and its angular methyl counterpart,[2] the dimethyldecalone **11** afforded only recovered starting material (98%) after 8 hr of reaction time. Evidently steric effects retard the postulated addition step of the cleavage reaction in this case. The apparent lesser reactivity of the cycloheptanone **3** and particularly the cyclooctanone **5** may be similarly explained. Likewise the conjugated keto thioketal **12** failed to yield a cleavage product. In this case a substantial pro-

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Experimental Section[6]

Thioketal Ketones

2,2-(Propane-1,3-dithio)cyclohexanone (1). - A solution of 1.64 g (13 mmol) of the hydroxymethylene ketone obtained (74%) from cyclohexanone by the procedure of Ainsworth,[7] 7.08 g (17 mmol) of propane-1,3-dithiol di-*p*-toluenesulfonate[8] and 5 g of potassium acetate in 100 ml of absolute ethanol was heated at reflux for 10 hr according to the procedure of Woodward.[6] The ethanol was removed *in vacuo* from the cooled reaction mixture. Water was added to the residue and the products were isolated with ether. The crude product was filtered through 70 g of Fisher alumina with 250 ml of benzene. Removal of the solvent afforded crystalline material which was recrystallized from ethanol affording 1.68 g (64%) of thioketal ketone 1. Recrystallization from ethanol and sublimation at 46° (0.02 mm) afforded material of mp 54-55°; λ_{max}^{KBr} 5.86 (CO), 6.96, 7.08, 7.86, 8.16, 8.96, 9.29, 10.62, 11.00, 11.44, 12.83, 13.61 μm.

Anal. Calcd for $C_9H_{14}OS_2$: C, 53.43; H, 6.97; S, 31.69. Found: C, 53.30; H, 6.94; S, 31.53.

2,2-(Propane-1,3-dithio)cycloheptanone (3). - The procedure outlined above for the preparation of thioketal ketone 1 was followed using 1.70 g of the hydroxymethylene ketone obtained (86%) from cycloheptanone by the procedure of Ainsworth.[7] The crude product was filtered through 70 g of Fisher alumina with 250 ml of benzene. Removal of the

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solvent afforded crystalline material which was recrystallized from ethanol affording 1.64 g (64%) of thioketal ketone 3. Recrystallization from ethanol and sublimation at 62° (0.02 mm) afforded material of mp 76.5-77.5°; λ_{max}^{KBr} 5.90 (CO), 6.90, 7.02, 7.65, 7.90, 8.10, 8.67, 8.81, 10.68, 11.05, 11.60, 11.80 μm.

Anal. Calcd for $C_{10}H_{16}OS_2$: C, 55.51; H, 7.45; S, 29.64. Found: C, 55.46; H, 7.48; S, 29.68.

2,2-(Propane-1,3-dithio)cyclooctanone (5). - The procedure outlined above for the preparation of thioketal ketone 1 was followed using 2.00 g of the hydroxymethylene ketone obtained (82%) from cyclooctanone by the procedure of Ainsworth.[7] The crude product was filtered through 70 g of Fishes alumina with 250 ml of benzene. Removal of the solvent afforded crystalline material which was recrystallized from ethanol affording 2.04 g (66%) of thioketal ketone 5. Recrystallization from ethanol and sublimation at 62° (0.02 mm) afforded material of mp 90-91°; λ_{max}^{KBr} 5.91 (CO), 6.85, 6.95, 7.01, 7.80, 7.81, 8.30, 8.61, 8.75, 9.00, 9.39, 11.00, 11.23, 11.78, 12.70 μm.

Anal. Calcd for $C_{11}H_{18}OS_2$: C, 57.35; H, 7.87; S, 27.83. Found: C, 57.28; H, 8.05; S, 27.70.

2,2-(Propane-1,3-dithio)-4-cyclohepten-1-one (7). - The procedure outlined above for the preparation of thioketal ketone 1 was followed using 2.35 g of the hydroxymethylene ketone obtained (88%) from 4-cycloheptenone[10] by the procedure of Ainsworth.[7] The crude product was

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filtered through 70 g of Fisher alumina with 250 ml of benzene. Removal of the solvent afforded crystalline material which was recrystallized from ethanol affording 2.40 g (66%) of thioketal ketone 7. Recrystallization from ethanol and sublimation at 66° (0.02 mm) afforded material of mp 83.5-84.5°; λ_{max}^{KBr} 5.90 (CO), 6.06, 7.01, 7.68, 7.89, 8.42, 9.86, 11.15, 11.50, 12.40, 13.52 μm; $\delta_{TMS}^{CDCl_3}$ 5.81 ppm ($H-C=C<^{H}$ multiplet).

Anal. Calcd for $C_{10}H_{14}S_2O$: C, 56.04; H, 6.58; S, 29.92. Found: C, 55.23; H, 6.66; S, 30.06.

3,3-(Propane-1,3-dithio)-10-methoxymethyl-*trans*-2-decalone (9). The procedure outlined above for the preparation of thioketal ketone 1 was followed using 4.50 g of the hydroxymethylene ketone obtained (94%) from 10-methoxymethyl-*trans*-2-decalone[2] by the procedure of Turner.[11] The crude product was filtered through 90 g of Fisher alumina with 500 ml of benzene. Removal of the solvent afforded crystalline material which was recrystallized from ethanol affording 5.32 g (89%) of thioketal ketone 9. Two additional recrystallizations from ethanol afforded material of mp 100-101°; λ_{max}^{KBr} 5.89 (CO), 6.70, 6.90, 7.08, 8.10, 8.55, 9.08, 9.95, 10.56, 11.01 μm; $\delta_{TMS}^{CDCl_3}$ 3.52 (2H, s) and 3.30 ppm (3H, s).

Anal. Calcd for $C_{16}H_{28}O_2S_2$: C, 59.96; H, 8.05; S, 21.34. Found: C, 60.13; H, 8.19; S, 21.45.

3,3-(Propane-1,3-dithio)-1,1-dimethyl-*trans*-2-decalone (11). - The procedure outlined above for the preparation of thioketal ketone 1 was followed using 3.70 g of the hydroxymethylene ketone obtained (93%) from 1,1-dimethyl-*trans*-2-decalone by the procedure of Turner.[11] The crude

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product was filtered through 70 g of Fisher alumina with 250 ml of benzene. *Removal of the solvent afforded crystalline material which was recrystallized* from ethanol affording 3.03 g (83%) of thioketal ketone 11. Two additional recrystallizations from ethanol afforded material of mp 95.5-97°; λ_{max}^{KBr} 5.92 (CO), 6.95, 7.05, 7.29, 7.39, 7.85, 9.45, 10.30, 11.05, 11.50, 12.55 μm; $\delta_{TMS}^{CDCl_3}$ 1.22 and 1.13 ppm (C-1 gem dimethyl).

Anal. Calcd for $C_{15}H_{24}OS_2$: C, 63.33; H, 8.50; S, 22.54. Found: C, 63.37; H, 8.65; S, 22.76.

3,3-(Propane-1,3-dithio)-10-methyl-1(9)-octal-2-one (12). The procedure outlined above for the preparation of thioketal ketone 1 was followed using 2.50 g of the hydroxymethylene ketone obtained (91%) from 10-methyl-1(9)-octal-2-one by the procedure of Turner.[11] The crude product was filtered through 70 g of Fisher alumina with 250 ml of benzene. Removal of the solvent afforded crystalline material which was recrystallized from ethanol affording 2.30 g (66%) of thioketal ketone 12. Two additional recrystallizations from ethanol afforded material of mp 127-128°; λ_{max}^{KBr} 6.09 (CO), 6.20, 7.05, 7.70, 7.90, 8.20, 8.40, 9.11, 10.51, 11.08, 11.55 μm; $\delta_{TMS}^{CDCl_3}$ 5.68 (1H, s) and 1.42 ppm (C-10 CH_3).

Anal. Calcd for $C_{14}H_{20}OS_2$: C, 62.64; H, 7.51; S, 23.89. Found: C, 62.42; H, 7.64; S, 23.78.

Cleavage Reactions

6,6-(Propane-1,3-dithio)hexanoic Acid (2). - To a stirred solution

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of thioketal ketone 1 (606 mg, 3 mmol) in 8 ml of *t*-butyl alcohol was added 504 mg (9 mmol) of powdered potassium hydroxide.[4] The reaction mixture was heated at 60° for 8 hr. Water was added and the aqueous phase was extracted with ether and acidified with cold conc hydrochloric acid. The acidic product was isolated by ether extraction affording 642 mg (97%) of crystalline solid. Recrystallization from ether-hexane yielded 615 mg (93%) of thioacetal acid 2. Recrystallization from ether-hexane and sublimation at 86° (0.02 mm) afforded material of mp 90-91.5°; λ_{max}^{KBr} 2.95-4.10(COOH), 5.91 (CO), 6.90, 7.03, 7.60, 7.89, 8.01, 8.20, 8.35, 8.52, 11.06, 13.15 μm; $\delta_{TMS}^{CDCl_3}$ 11.38 (COOH, s) and 4.01 ppm (1H, t, J=6 Hz).

Anal. Calcd for $C_9H_{16}O_2S_2$: C, 49.06; H, 7.32; S, 29.10. Found: C, 49.17; H, 7.20; S, 29.24.

The identical material was obtained in 92% yield by treatment of thioketal ketone 1 with a 3-fold excess of KO*t*-Bu (0.3 *M*) to which an equivalent amount of water was added prior to stirring at 60° for 8 hr.

7,7-(Propane-1,3-dithio)heptanoic Acid (4). - The procedure outlined above for the preparation of thioacetal acid 2 was followed using 648 mg of thioketal ketone 3. The reaction mixture was heated at 60° for 10 hr. The crude product (699 mg, 99%) was recrystallized from ether-hexane yielding 687 mg (95%) of thioacetal acid 4. Recrystallization from ether-hexane and sublimation at 88°(0.02 mm) afforded material of mp 74-75°; λ_{max}^{KBr} 3.02-4.10 (COOH), 5.89 (CO), 6.88, 7.02, 7.15, 7.88, 8.07, 11.06 μm; $\delta_{TMS}^{CDCl_3}$ 10.80 (COOH, s) and 4.00 ppm (1H, t, J=6 Hz).

Anal. Calcd for $C_{10}H_{18}O_2S_2$: C, 51.25; H, 7.74; S, 27.36. Found: C, 51.18; H, 7.66; S, 27.37.

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8,8-(Propane-1,3-dithio)octanoic Acid (6). - The procedure outlined above for the preparation of thioacetal acid 2 was followed using 960 mg of thioketal ketone 5. The reaction mixture was heated at 60° for 48 hr. The isolation procedure afforded 998 mg (96%) of crude acid. Part (120 mg) of the crude acid was chromatographed on 10 g of silica gel with ether as eluant yielding 109 mg of thioacetal acid 6. Recrystallization from ether-hexane afforded material of mp 90-91°; λ_{max}^{KBr} 2.80-4.10 (COOH), 5.85 (CO), 6.80, 6.99, 7.10, 8.00, 8.10, 8.20, 11.00, 12.25 μm; $\delta_{TMS}^{CDCl_3}$ 9.41 (COOH, s) and 4.00 ppm (1H, t, J=6 Hz).

Anal. Calcd for $C_{11}H_{20}O_2S_2$: C, 53.19; H, 8.12; S, 25.82. Found: C, 53.42; H, 8.19; S, 25.80.

(Z)-7,7-(Propane-1,3-dithio)-4-heptenoic Acid (8). - The procedure outlined above for the preparation of thioacetal acid 2 was followed using 842 mg of thioketal ketone 7. The reaction mixture was heated at 60° for 10 hr. The crude product (699 mg, 100%) was recrystallized from ether-hexane yielding 648 mg (93%) of thioacetal acid 8. Recrystallization from ether-hexane and sublimation at 82° (0.02 mm) afforded material of mp 57-58°; λ_{max}^{KBr} 2.85-4.10 (COOH), 5.89 (CO), 7.05, 7.15, 7.78, 7.90, 8.30, 10.80, 12.90 μm; $\delta_{TMS}^{CDCl_3}$ 11.59 (COOH, s), 5.50 (2H, t, J=5 Hz) and 4.02 ppm (1H, t, J=6 Hz).

Anal. Calcd for $C_{11}H_{18}S_2O_2$: C, 51.92; H, 6.54; S, 27.72. Found: C, 51.86; H, 6.75; S, 27.65.

1-[2,2-(Propane-1,3-dithio)ethyl]-*cis*-1-methoxymethylcyclohex-2-yl Acetic Acid (10). - The procedure outlined above for the preparation of thioacetal acid 2 was followed using 800 mg of thioketal ketone 9. The

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reaction mixture was heated at 60° for 12 hr. The crude product (664 mg, 100%) was recrystallized from ether-hexane yielding 565 mg (92%) of thioacetal acid 10. An additional recrystallization from ether-hexane afforded material of mp 97-97.5°; λ_{max}^{KBr} 2.80-4.10 (COOH), 5.88 (CO), 6.95, 7.09, 7.71, 7.89, 8.08, 8.40, 9.05, 10.68, 11.02 μm; $\delta_{TMS}^{CDCl_3}$ 11.80 (COOH, s), 4.00 (1H, t, J=6 Hz) and 3.22 ppm (5H, s).

Anal. Calcd for $C_{15}H_{26}O_3S_2$: C, 56.75; H, 7.94; S, 20.20. Found: C, 56.93; H, 8.24; S, 19.91.

Attempted Cleavage of Thioketal Ketone 11. - The procedure outlined above for the preparation of thioacetal acid 2 was followed using 426 mg of thioketal ketone 11. The reaction mixture was heated at 60° for 6 hr. The neutral extracts afforded 417 mg (98%) of starting material.

Attempted Cleavage of Thioketal Ketone 12. - The procedure outlined above for the preparation of thioacetal acid 2 was followed using 402 mg of thioketal ketone 12. The reaction mixture was heated at 60° for 8 hr. The neutral extracts afforded 379 mg (94%) of a mixture of starting material (20%) and the β-γ-unsaturated isomer 13 (80%) of the starting material as determined by analysis of the infrared and nmr spectra.

Attempted Cleavage of 2-Thiophenylcyclohexanone (14).[12] - The procedure outlined above for the preparation of thioacetal acid 2 was followed using 618 mg of α-thiophenyl ketone 14. The reaction mixture was heated at 60° for 20 hr. The neutral extracts afforded 615 mg (99%) of starting material.

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Attempted Cleavage of 2-Methyl-2-thiophenylcyclohexanone (15).[13] - The procedure outlined above for the preparation of thioacetal acid 2 was followed using 440 mg of α-thiophenyl ketone 15. The reaction mixture was heated at 60° for 10 hr. The neutral extracts afforded 439 mg (100%) of starting material.

6,6-bis-Thiophenylhexanoic Acid (17). - The procedure outlined above for the preparation of thioacetal acid 2 was followed using 785 mg of *2,2-bis*-thiophenylcyclohexanone (16).[12] The reaction mixture was heated at 60° for 10 hr. The isolation procedure afforded 573 mg (69%) of crude acid. A 246-mg sample of this material was chromatographed on 20 g of silica gel with ether as eluant yielding 232 mg of thioacetal acid 17 which was distilled at 185°(bath temp) and 0.01mm; λ_{max}^{film} 2.80-4.10 (COOH), 5.87 (CO), 6.31, 6.79, 6.99, 9.20, 9.40, 9.79, 13.50, 14.35 μm; $\delta_{TMS}^{CDCl_3}$ 10.20 (COOH, s), 6.90-7.55 (10H, m) and 4.30 ppm (1H, t, J=6 Hz).

Anal. Calcd for $C_{18}H_{20}O_2S_2$: C, 65.03; H, 6.06; S, 19.29. Found: C, 65.09; H, 6.17; S, 19.09.

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Illinois. Infrared spectra were obtained with a Perkin-Elmer 137 spectrophotometer. Infrared absorption are reported in wavelengths (μm) and are standardized with reference to the 6.24-μm peak of polystyrene. Nuclear magnetic resonance spectra were recorded with a Varian T-60 spectrometer. Signals are reported as the chemical shift downfield from tetramethylsilane (TMS) in parts per million (ppm) of the applied field. The multiplicity of the peak is abbreviated: singlet s, doublet d, triplet t, quartet q and multiplet m. Coupling constants are reported in herts (Hz). Melting points were determined on a calibrated Thomas capillary melting point apparatus. Melting points are not corrected.

References

6. The apparatus described by W. S. Johnson and W. P. Schneider ("Organic Syntheses," Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1963, p. 132] was used to maintain an argon atmosphere. The isolation procedure consisted of thorough extractions with the specified solvent, washing the combined extracts with saturated brine solution, and drying the extracts over anhydrous magnesium sulfate. The solvent was removed from the filtered extracts under reduced pressure on a rotary evaporator. Microanalyses were performed by Micro-Tech Laboratories, Inc., Skokie,
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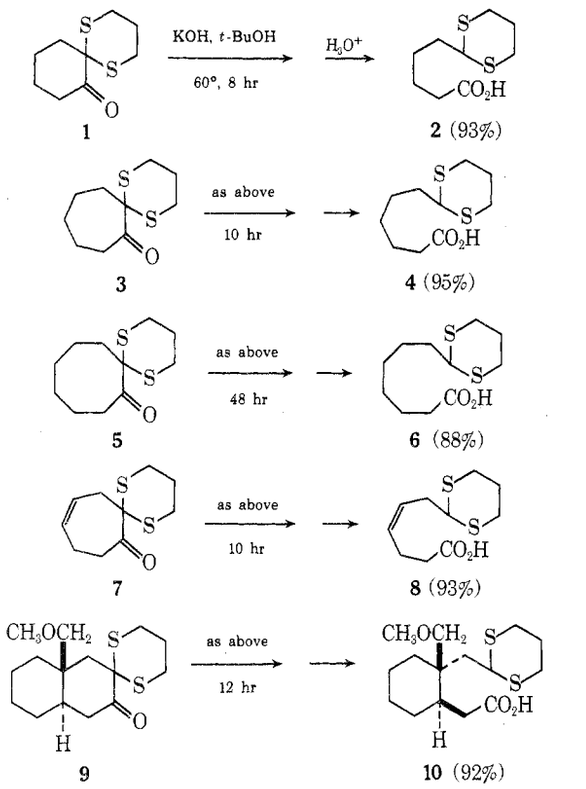
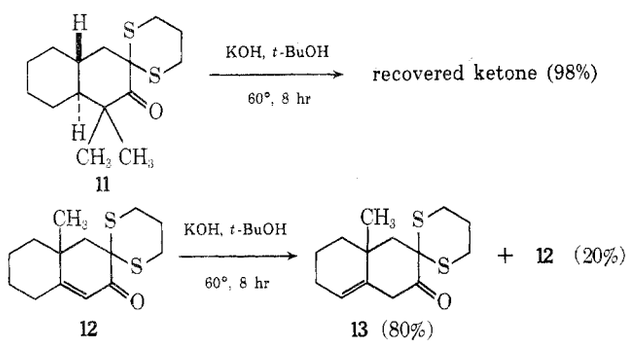
Chart I

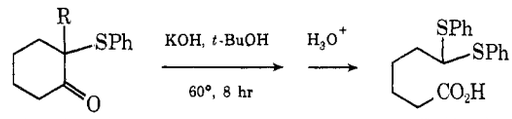


portion of the recovered material appeared to be the β,γ-unsaturated isomer **13**. Thus, enolate formation evidently



retards addition to the conjugated carbonyl group. Neither of the above uncooperative keto thioketals **11** or **12** could be induced to yield acidic cleavage products. Prolonged reaction times merely led to their gradual destruction.

Attempts to extend the cleavage reaction to α-thiophenyl ketones did not appear promising. Both cyclohexanone derivatives **14** and **15** were unaffected by the KOH–*t*-BuOH treatment. However with 2,2-bis(thiophenyl)cyclohexanone (**16**) cleavage did take place to give the acid **17** in 66% yield.



14, R = H
15, R = CH_3
16, R = SPh

Trost and coworkers have recently described the facile cleavage of the thioketal derivatives of cyclobutane-1,2-diones and the related alcohols with methanolic sodium methoxide to give β-1,3-dithianyl esters and ketones.[5] Under these conditions both the thioketal ketone **1** and the alcohol obtained upon addition of methyllithium to ketone **1** were recovered unchanged after 10 hr at reflux. Thus, as noted by Trost, ring strain must provide substantial driving force for the cyclobutane cleavage reactions.

Finally, cleavage of the thioketal ketone **1** to acid **2** also took place efficiently (92% yield) upon treatment with excess potassium *tert*-butoxide in *tert*-butyl alcohol to which the equivalent amount of water was added. Interestingly, with methanolic potassium hydroxide only starting thioketal ketone **1** was recovered after 8 hr at 60°.

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Registry No.—**1**, 51310-03-3; **2**, 51310-04-4; **3**, 51310-05-5; **4**, 51310-06-6; **5**, 51310-07-7; **6**, 51364-41-1; **7**, 51364-42-2; **8**, 51310-08-8; **9**, 42836-58-8; **10**, 51310-09-9; **11**, 51310-10-2; **12**, 51310-11-3; **13**, 51310-12-4; **16**, 35874-99-8; **17**, 51310-13-5; cyclohexanone hydroxymethylene derivative, 823-45-0; cycloheptanone hydroxymethylene derivative, 934-20-3; cyclooctanone hydroxymethylene derivative, 936-65-2; 4-cycloheptenone hydroxymethylene derivative, 51310-14-6; 10-methoxymethyl-*trans*-2-decalone hydroxymethylene derivative, 51310-15-7; 1,1-dimethyl-*trans*-2-decalone hydroxymethylene derivative, 51310-16-8; 10-methyl-1(9)-octal-2-one hydroxymethylene derivative, 5240-82-4.

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References and Notes

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