eoselection at the 5-position of 1,3-diheterocyclohexanes. Other workers have found diastereoselection at the 2-position of six-membered heterocycles. Eliel and Nader[10] found a preponderance of axial attack by alkylmagnesium halides on the carbocation formed at the 2-position of 1,3-dioxanes. Anancomeric 1,3-dithianes gave equatorial 2-substituted compounds upon treatment with DCl, CH_3I, or carbonyl compounds.[11]

Experimental Section

2-Isopropyl-5,5-bis(carboethoxy)-1,3-dioxane was prepared by following the procedure of Eliel and Banks.[16] 2-Isopropyl-5,5-bis(carbomethoxy)-1,3-dioxane was prepared in a similar manner except that dimethyl malonate was substituted for diethyl malonate.

Diethyl 4-*tert*-Butylcyclohexane-1,1-dicarboxylate. 4-*tert*-Butylcyclohexanecarboxylic acid was prepared by following the procedure of Stolow.[12] The acid (11.5 g, 62.4 mmol) was mixed with thionyl chloride (10.5 mL, 144 mmol) and allowed to stand at room temperature for 15 min; the reaction mixture was then refluxed for 15 min. The excess thionyl chloride was removed under reduced pressure. Pyridine (20 mL) was added, followed by the dropwise addition of absolute ethanol (20 mL, 348 mmol). After 0.5 h of reflux, the reaction mixture was poured into an ice–water mixture and extracted three times with 50-mL portions of diethyl ether. The combined ethereal extracts were washed with saturated aqueous $NaHCO_3$ and saturated NaCl and were dried over anhydrous $MgSO_4$. Filtration and concentration on the rotary evaporator gave 9.72 g (73.5%) of ethyl 4-*tert*-butylcyclohexanecarboxylate, bp 98–104 °C (1.4 mm) [lit.[13] (cis) bp 102–103 °C (9 mm), (trans) bp 106–107 °C (10 mm)].

Ethyl 4-*tert*-butylcyclohexanecarboxylate (8.00 g, 37.7 mmol) was converted to 4-*tert*-butyl-1-(carboethoxy)cyclohexanecarboxylic acid (6.54 g 67.3%) by following the procedure of Reffers.[14] This half-ester was then treated with thionyl chloride as above, followed by ethanol and pyridine. The product was isolated in 54.0% yield (3.91 g), bp 90–91 °C (0.08 mm) [lit.[15] bp 132 °C (2.5 mm)].

7-Oxa-2,2-bis(carbomethoxy)bicyclo[2.2.1]heptane. A magnetically stirred solution of 10 mL of anhydrous Et_2O, 40 mL of CH_2Cl_2, 45.1 mL (43.1 g, 500 mmol) of methyl acrylate, and 35.8 mL (33.5 g, 492 mmol) of furan was treated with small portions of a total of 0.6 g of $AlCl_3$ over a 10-min period. The reaction vessel was fitted with a reflux condenser, placed in a water bath at 23 °C, and allowed to stand for 72 h. A total of 25 mL of H_2O was added in small portions. The dark brown reaction mixture changed to a light brown after being stirred for 2 h and was then filtered through a fritted disk. The two-phase system was separated and the organic layer was dried over a mixture of anhydrous $MgSO_4$ and Na_2CO_3. The dry solution was filtered and concentrated under reduced pressure. A portion (22.43 g) of the above residue was dissolved in 250 mL of 95% ethanol, and 100 mg of 10% Pd/C was added. Hydrogenation was effected by using a Parr apparatus with an initial pressure of 47 psi. After removal of the catalyst and collection of a low-boiling fraction (1.0 mL), a fraction was collected: 17.4 g (77.6%); bp 92–94 °C (6.2 torr); ^1H NMR[17] (CCl_4) δ 1.29–2.10 (m, 6 H), 2.3–3.02 (m, 1 H), 3.14 (s, 1 H), 4.36–4.79 (m, 2 H).

By the procedure of Reffers et al,[14] diisopropylamine (3.0 g, 4.2 mL, 30.0 mmol) in 30 mL of dry tetrahydrofuran (THF), 15 mL of 2.3 M *n*-butyllithium, and 7-oxa-2-(carbomethoxy)bicyclo[2.2.1]heptane (4.00 g, 25.6 mmol) in 20 mL of THF were used to prepare 7-oxa-2-carboxy-2-(carbomethoxy)bicyclo[2.2.1]heptane. This half-ester was treated with 2 mL of $SOCl_2$ and the magnetically stirred mixture was heated to the boiling point. The hot reaction product was concentrated with an aspirator and cooled in an ice–water bath, and 2 mL of pyridine and methanol were added. After standing for 8 h at room temperature, the reaction mixture was poured into ice–water, extracted three times with a total of 25 mL of Et_2O, dried over $MgSO_4$, filtered, and distilled to give 1.0 g (18.2%) of product: bp 57–61 °C (0.15 torr); ^1H NMR (CCl_4) δ 1.30–1.44 (m, 6 H), 2.13–2.97 (m, 3 H), 3.59 (s, 3 H), 4.36–4.72 (m, 2 H).

Decarbalkoxylations. These reactions were conducted either in sealed ampoules in a constant-temperature bath (±0.1 °C) or in round-bottomed flasks equipped with condensers and $CaCl_2$ drying tubes in silicone oil baths (±1 °C). Typical procedures follow.

1. Decarboethoxylation of 2-Isopropyl-5,5-bis(carboethoxy)-1,3-dioxane. A mixture of 80.64 mg (1.902 mmol) of LiCl, 54.9 mg (3.053 mmol) of H_2O, 383.0 mg (1.398 mmol) of 2-isopropyl-5,5-bis(carboethoxy)-1,3-dioxane, 152.3 mg (0.8948 mmol), and 5 μL of pyridine was dissolved in 2.00 mL of dimethyl sulfoxide. Samples of 200 μL of this solution were sealed into small ampules constructed from 6-mm glass tubing and were then placed into a silicone oil bath maintained at 135.0 ±0.1 °C. Ampules were withdrawn periodically, cooled, and opened. A Pasteur pipet was used to transfer the contents of the ampule to a vial containing 2 mL of 5% aqueous $KHCO_3$. The mixture was extracted three times with 1-mL portions of Et_2O. The combined ethereal extracts were dried over a mixture of anhydrous $MgSO_4$ and Na_2CO_3. The dried solution was analyzed by GLC [6 ft × 0.25 in 20% FFAP on Chromosorb W, 80–100 mesh, He flow 100 mL/min, program mode 180 (4 min), 180–210 (3 min), 210 °C (4 min)].

2. Decarboethoxylation of Diethyl 4-*tert*-Butylcyclohexane-1,1-dicarboxylate. A mixture of LiCl (40.9 mg, 01965 mmol), H_2O (46.1 mg, 2.56 mmol), diphenyl ether (102.7 mg, 0.603 mmol, internal standard), 5 μL of pyridine, and 1.00 mL of dimethyl sulfoxide was added to a 25-mL flask equipped with a magnetic stirring bar, condenser, and $CaCl_2$ drying tube. The mixture was heated to 135 ±1 °C by means of a silicone oil bath. By means of a syringe, 209.6 mg (0.738 mmol) of 4-*tert*-butyl-1,1-bis(carboethoxy)cyclohexane was added at such a rate that thermal equilibrium was maintained. Samples were removed periodically and quenched by addition to 1 mL of 5% aqueous Na_2CO_3. The resulting mixture was worked up and analyzed as above.

Control experiments demonstrated that the product composition was unaffected by the workup procedure.

Registry No. 1, 35113-48-5; 1 (R_2, R_3 = $COOCH_3$), 76480-24-5; 2, 70708-55-3; 3, 70708-56-4; 4, 53695-41-3; 5, 7214-36-0; 6, 7214-35-9; 7, 76480-25-6; 4-*tert*-butylcyclohexanecarboxylic acid, 5451-55-8; 4-*tert*-butyl-1-(carboethoxy)cyclohexanecarboxylic acid, 76480-26-7; methyl acrylate, 96-33-3; furan, 110-00-9; *endo*-7-oxa-2-(carbomethoxy)bicyclo[2.2.1]heptane, 17791-35-4; *exo*-7-oxa-2-(carbomethoxy)-bicyclo[2.2.1]heptane, 17791-34-3; 7-oxa-2-carboxy-2-(carbomethoxy)bicyclo[2.2.1]heptane, 76480-27-8.

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Phase Transfer Catalyzed Hydrolysis of Thioacetals Using Pyridinium Hydrobromide Perbromide

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In connection with some ongoing studies, we required a mild, general method for the hydrolysis of various α-thioketalized aldehydes,[2] carboxylic acids,[3] and esters[4] to

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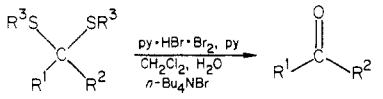
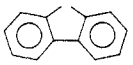
Table I. Hydrolysis of Thioacetals with Pyridinium Hydrobromide Perbromide[a,b]



entry	R^1	R^2	R^3	% yield	ref for thioacetal
1	n-C_6H_{13}	H	$-(CH_2)_3-$	78	9
2	$CH_3(CH_2)_7CH{=}CH(CH_2)_7$	H	$-(CH_2)_3-$	87	10
3	C_6H_5	H	$-(CH_2)_3-$	87	11
4	n-C_9H_{19}	CH_3	$-(CH_2)_3-$	83	10
5	n-C_4H_9	n-C_4H_9	$-(CH_2)_3-$	80	10
6	$-(CH_2)_5-$		$-(CH_2)_3-$	83	12
7	C_6H_5	CH_3	$-(CH_2)_3-$	80	13
8			$-(CH_2)_3-$	91	14
9	n-C_4H_9	$CO_2C_2H_5$	$-(CH_2)_3-$	81	4a
10	n-C_4H_9	$CO_2C_2H_5$	C_2H_5	80	4b
11	CH_3	$CH{=}CHCO_2CH_3$	C_2H_5	83	10
12	n-C_4H_9	CO_2H	C_2H_5	74[c]	3b
13	n-C_4H_9	CHO	C_2H_5	80	2, 10

[a] Complexes 1 and 2 may be used interchangeably. [b] Yields are of purified isolated material. [c] Reaction carried out in aqueous acetonitrile (no pyridine).

the corresponding α-dicarbonyl compounds. In addition, such a method might also be a useful complement to the existing methods of thioketal hydrolysis.[5] We have found that a wide range of thioacetals and thioketals including monothioketals of various α-dicarbonyl compounds may be conveniently hydrolyzed to the corresponding carbonyl compounds in excellent yields in a mixture of dichloromethane and water containing *1* molar equiv of pyridinium hydrobromide perbromide complex 1[6a] (or 0.5 molar equiv of complex 2[6b]), 1 molar equiv of pyridine, and 0.1 molar

$C_5H_5N{\cdot}HBr{\cdot}Br_2$ (1) $\qquad$ $(C_5H_5N{\cdot}HBr)_3{\cdot}(Br_2)_2$ (2)

equiv of tetrabutylammonium bromide as a phase-transfer catalyst.[7] The hydrolysis of a wide variety of thioacetals and thioketals is summarized in Table I. It is significant to note that neither alkene (entries 2, 11) nor aromatic (entries 3, 7, 8) derivatives are brominated under the reaction conditions. The reaction is both simple to carry out as well as convenient to work up (see Experimental Section).

The reaction system described above is, however, unsatisfactory for the hydrolysis of α-thioketalized acids. Nevertheless, the hydrolysis may be carried out by dropwise addition of a solution of either of the bromine complexes to a solution of the acid in aqueous acetonitrile (no pyridine). This solvent system may be used (with or without pyridine) for the hydrolysis of many of the other compounds listed in Table I; however, the yields of carbonyl compounds are usually 5–25% lower than when the phase-transfer method is employed.

The pyridine used in the two-phase reaction system not only buffers the reaction medium but is necessary for effective action of the phase-transfer catalyst. In contrast to other thioketal hydrolysis methods only *1* equiv of an oxidizing agent is required. Higher yields of product are not observed when the amount of pyridinium complex is increased.

Experimental Section

General Procedures. All reactions were carried out under a nitrogen or argon atmosphere. Stirring was accomplished by using Teflon-covered magnetic stirring bars.

All aldehydes (ketones) were converted into the corresponding dithianes by using the general method of Seebach and Corey.[8] Oleyl aldehyde was prepared by pyridinium chlorochromate oxidation of oleyl alcohol. Literature procedures were followed for the preparation of α-thioketalized aldehydes,[2] acids,[3b] and esters.[4] The α,β-unsaturated system (entry 11) was prepared via a Wadsworth–Emmons reaction on the corresponding α-thioketalized aldehyde. All reagents were obtained from the Aldrich Chemical Company, Inc., and were used without further purification.

All compounds had elemental analyses and IR, NMR, and mass spectra fully consistent with the proposed structures. The physical data of several previously unreported thioacetals are given below. Proton magnetic resonance spectra were obtained on Varian Associates T-60 and HA-100 spectrometers. Spectra were run in deuteriochloroform solution with tetramethylsilane as an internal reference. The multiplicity, integrated peak area, and coupling constants (hertz, if observable) are indicated in parentheses after each signal. Infrared spectra were recorded in chloroform solution, using a Perkin-Elmer 700 spectrometer, and were calibrated with the 1601-cm^{-1} band of polystyrene. High-resolution mass spectra were obtained by using an AE1 MS-50 spectrometer. Elemental analyses were performed at the Microanalytical Laboratory, University of British Columbia. The recovered carbonyl compounds were purified and compared with samples of authentic material. Compounds were checked for

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purity by using thin-layer and gas–liquid chromatography.

Preparation and Analysis of Pyridinium Hydrobromide Perbromide Complexes. Complex 1 could be prepared according to the method of Fieser.[6a] The complex is also available from Aldrich Chemical Company, Inc. Recrystallization of 10 g of the crude complex from 5.5 mL of acetic acid yields 7.5 g of pure material melting at 132–34 °C. Anal. Calcd for $C_5H_5N{\cdot}HBr{\cdot}Br_2$: reducible Br, 49.96; total Br, 74.95. Found: reducible Br, 49.9; total Br, 75.0. Complex 2 could be prepared according to the method of Englert and McElvain.[6b] Complex 1 may also be converted into complex 2. Recrystallization of 10 g of complex 1 from 8.5 mL of acetic acid yields 8.2 g of complex 2 melting at 104–106 °C. Anal. Calcd for $3(C_5H_5N{\cdot}HBr){\cdot}2Br_2$: reducible Br, 39.97; total Br, 69.95. Found: reducible Br, 39.9; total Br, 70.4.

General Procedure for Hydrolysis of Thioacetals and Thioketals. (a) Phase-Transfer Method. (This method is preferred in most cases.) With vigorous stirring, 1 mmol of tetrabutylammonium bromide was added to a mixture of 10 mmol of thioacetal, 10 mmol of pyridine, and 10 mmol of complex 1 (or 5 mmol of complex 2) in 10 mL of dichloromethane and 2 mL of water at 0 °C.

The red-orange color of the bromine complex faded to colorless or a pale yellow within a few minutes. Stirring was continued at room temperature for 2 h to complete the hydrolysis. The dichloromethane layer was separated and the aqueous phase was extracted with two 10-mL portions of dichloromethane. The combined organic phase was washed with water and then was filtered through a loose cotton plug to remove suspended water. The solvent was evaporated and the crude carbonyl compound was purified by distillation or chromatography through a short column of Florisil to yield essentially (>98%) pure material.

(b) Aqueous Acetonitrile. (This procedure is recommended for α-thioketalized acids.) A solution of 10 mmol of bromine complex 1 (or 5 mmol of complex 2) in 2 mL of aqueous 50% acetonitrile was added dropwise at 0 °C to a stirred solution of 10 mmol of thioacetal dissolved in 15 mL of aqueous 10% acetonitrile. Pyridine (1 equiv) may be added to the reaction mixture if desired. Hydrolysis to give an α-keto acid should be carried out in the absence of pyridine. The orange color of the bromine complex rapidly discharges to colorless or a pale yellow. The reaction mixture was stirred at room temperature for 30 min. After the acetonitrile had been evaporated, the residue was taken up in ether, washed with water, and dried over anhydrous magnesium sulfate. The ether was evaporated and the crude carbonyl compound purified as above.

2-(Heptadec-8-enyl)-1,3-dithiacyclohexane: NMR δ 0.9 (t, 3, J = 7), 1.1–1.8 (br m, 26), 1.8–2.4 (m, 4), 2.8–2.95 (m, 4), 4.05 (t, 1, J = 6), 5.4 (t, 2, J = 5); mol wt calcd for $C_{21}H_{40}S_2$ 356.2571, found 356.2568. Anal. Calcd for $C_{21}H_{40}S_2$ (mol wt 356.68): C, 70.72; H, 11.30; S, 17.98. Found: C, 70.55; H, 11.25; S, 17.81.

2-Methyl-2-nonyl-1,3-dithiacyclohexane: NMR δ 0.85 (t, 3, J = 7), 1.1–1.5 (br m, 14), 1.6 (s, 3), 1.8–2.1 (m, 4), 2.8 (t, 4, J = 6); mol wt calcd for $C_{14}H_{28}S_2$ 260.1633, found 260.1633. Anal. Calcd for $C_{14}H_{28}S_2$ (mol wt 260.51): C, 64.55; H, 10.83; S, 24.62. Found: C, 64.29; H, 10.77; S, 24.71.

2,2-Dibutyl-1,3-dithiacyclohexane: NMR δ 0.9 (t, 6, J = 7), 1.2–1.5 (m, 8), 1.8–2.0 (m, 6), 2.75 (t, 4, J = 6); mol wt calcd for $C_{12}H_{24}S_2$ 232.1319, found 232.1320. Anal. Calcd for $C_{12}H_{24}S_2$ (mol wt 232.45): C, 62.00; H, 10.41; S, 27.59. Found: C, 62.05; H, 10.33; S, 27.41.

(*E*)-Methyl 4,4-bis(ethylthio)pent-2-enoate: IR 1645, 1725 cm^{-1}; NMR δ 1.1 (t, 6, J = 7), 1.6 (s, 3), 2.5 (q, 4, J = 7), 3.6 (s, 3), 5.7 (d, 1, J = 16), 6.7 (d, 1, J = 16); mol wt calcd for $C_{10}H_{18}O_2S_2$ 234.0748, found 234.0746. Anal. Calcd for $C_{10}H_{18}O_2S_2$ (mol wt 234.38): C, 51.25; H, 7.74; S, 27.36. Found: C, 51.11; H, 7.69; S, 27.30.

2,2-Bis(ethylthio)hexanal: IR 1710 cm^{-1}; NMR δ 0.8–2.0 (m, 15), 2.4 (q, 4, J = 7), 8.75 (s, 1); mol wt calcd for $C_{10}H_{20}OS_2$ 220.0955, found 220.0956. Anal. Calcd for $C_{10}H_{20}OS_2$ (mol wt 220.40): C, 54.50; H, 9.15; S, 29.10. Found: C, 54.25; H, 9.13; S, 28.78.

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Registry No. 1, 39416-48-3; 2, 53913-80-7; 2-hexyl-1,3-dithiane, 26958-42-9; (*Z*)-8-heptadecenyl-1,3-dithiane, 76467-37-3; 2-phenyl-1,3-dithiane, 5425-44-5; 2-methyl-2-nonyl-1,3-dithiane, 70499-19-3; 2,2-dibutyl-1,3-dithiane, 76467-38-4; 1,5-dithiaspiro[5.5]undecane, 180-59-6; 2-methyl-2-phenyl-1,3-dithiane, 6331-22-2; spiro[1,3-dithiane-2,9′-[9H]fluorene], 165-06-0; ethyl 2-butyl-1,3-dithiane-2-carboxylate, 32557-27-0; ethyl 2,2-bis(ethylthio)hexanoate, 76467-39-5; methyl(*E*)-4,4-bis(ethylthio)pent-2-enoate, 76467-40-8; 2,2-bis(ethylthio)hexanoic acid, 71535-47-2; 2,2-bis(ethylthio)hexanal, 76371-99-8; heptanal, 111-71-7; (*Z*)-9-octadecenal, 2423-10-1; benzaldehyde, 100-52-7; 2-undecanone, 112-12-9; 5-nonanone, 502-56-7; cyclohexanone, 108-94-1; 1-phenylethanone, 98-86-2; 9*H*-fluoren-9-one, 486-25-9; ethyl 2-oxohexanoate, 5753-96-8; methyl *trans*-4-oxo-2-pentenoate, 2833-24-1; 2-oxohexanoic acid, 2492-75-3; 2-oxohexanal, 2363-84-0.

Synthesis and Conformational Mobility of [2.2](2,6)Pyridinophan-1-ene

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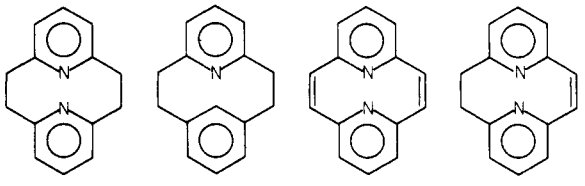
There has been considerable interest in the synthesis and properties of [2.2]metacyclophanes over the past two decades.[1] Many of these cyclophanes have proven highly useful in investigations of steric interactions through studies of the effects of substituents on the rates of conformational processes.[2] Particularly intriquing are the pyridinophanes 1 and 2 where conformational flipping



1 2 3 4

involves lone pair–lone pair and lone pair–CH interactions, respectively. In the former case, $\Delta G^{\ddagger}$ = 14.8 kcal/mol has been reported[3] for the conformational interchange while the value for 2 is too large for determination by the dynamic NMR technique.[4] Boekelheide has reported the preparation of diene 3 and suggests that the ethylene bridges render this cyclophane conformationally rigid based on the absence of NMR spectral changes over a wide temperature range.[5] The absence of nonequivalent exchange sites in this molecule makes this interpretation questionable, however. We report the synthesis [2.2]-(2,6)pyridinophan-1-ene (4) and more definitive results from dynamic NMR studies of its conformational behavior.

While a number of [2.2]cyclophanedienes are known,[5,6] compounds with single ethylenic bridges are relatively rare,[7] especially in heterocyclic systems.[6b] the usual strategy for construction of such systems involves ring

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