theoretical); $[\alpha]^{24}_D$ +2° (c 2.65, $CHCl_3$); mp 57-59 °C; IR (KBr) 2940, 1380, 1270, 970 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.89 (1 H, ddt, J = 13.0, 11.2, 3.5 Hz), 1.10 (3 H, s), 1.16 (3 H,s), 1.38 (3 H, s), 1.58 (3 H, br s), 1.59 (3 H, br s), 4.81 (1 H, dd, J = 12.3, 5.2 Hz), 4.87 (1 H, br d, J = 11.0 Hz), 5.27 (1 H, br d, J = 8.0 Hz); mass spectrum (CI, isobutane), m/e 369 (MH^+, $C_{20}H_{33}BrO$, 21), 367 (31), 352 (8), 350 (11), 288 (100), 270 (37).

Treatment of Bromide 11 with Silver Perchlorate. Aqueous solution (0.4 mL) of silver perchlorate (100 mg) was added to a stirred solution of bromide 11 in acetone (0.8 mL). After 1 h at room temperature the solution was filtered to remove salts, and the solvent was evaporated. The residue was chromatographed on silica gel H to obtain the enol ether **10**: 39 mg (65% theoretical); $[\alpha]^{24}_D$ +9° (c 3.0, $CHCl_3$); identical in all respects with the same compound obtained from alcohol **4**.

Ozonolysis of α-Terpinol. Ozone in oxygen was bubbled through a solution of α-terpinol (1.54 g) in ethyl acetate (100 mL) which had been cooled to -78 °C. After 10 min, the excess reagent was removed by warming the solution to room temperature. Following the usual oxidative workup with 30% aqueous H_2O_2 (2 mL), a 1:1 mixture of two epimeric lactols was obtained: 1.73 g (93% theoretical); IR (neat) 3480, 2990, 1710, 1370, 1170 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 0.85 (3 H, s), 1.00 (3 H, s), 1.10 (3 H, s), 1.25 (3 H, s), 2.05 (6 H, s), 5.40 (2 H, m); ^{13}C NMR (22.63 MHz, $CDCl_3$) δ 208.0, 106.4, 105.3, 84.9, 83.6, 47.5, 45.5, 42.6, 35.9, 35.6, 30.0, 29.2, 27.8, 23.9, 23.4, 22.9. Jones reagent (1 mL) was added to a solution of the above lactols mixture (1.50 g) in acetone (20 mL). After 10 min, a few drops of methanol were added to destroy excess reagent, and the solvent was evaporated. The residue was partitioned between water (10 mL) and dichloromethane (3 × 20 mL). The dichloromethane phase was dried over magnesium sulfate and then evaporated to yield the homoterpenyl methyl ketone **12**: 1.47 g (97% theoretical); IR (CCl_4) 2990, 2970, 1760, 1705, 1420, 1390, 1375, 1270, 1255, 1165, 1125, 1000, 955, 935, 915 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 1.20 (3 H, s), 1.40 (3 H, s), 2.05 (3 H, s), 2.30 (4 H, m); ^{13}C NMR (22.63 MHz, $CDCl_3$ δ 207.6 (s), 175.4 (s), 86.7 (s), 45.0 (d), 41.7 (t), 34.6 (t), 29.9 (q), 27.3 (q), 23.1 (t), 21.3 (q).

Ozonolysis of Naphthenol (2). Ozonolysis of nephthenol in the same manner as described for α-terpinol gave the same homoterpenyl methyl ketone (**12**).

Microozonolysis[4] of Enol Ether 10. Ozone in oxygen was bubbled through a solution of compound **10** (10 mg) in dichloromethane (10 mL) which had been cooled to -78 °C. After 10 min, the excess reagent was removed by warming the solution to room temperature, and triphenylphosphine (20 mg) was added to the stirred solution. Analysis of the reaction mixture by GC[4] indicated the presence of **12** (identical with **12** which had been obtained from α-terpinol and nephthenol) and levulinaldehyde (identical with an authentic sample).

Treatment of 13 with p-Toluenesulfonic Acid. A solution of **13** (40 mg) and p-toluenesulfonic acid (0.5 mg) in chloroform (2 mL) was kept for 24 h at room temperature. The chloroform solution was then washed with aqueous sodium bicarbonate solution and dried over anhydrous $MgSO_4$. The solvent was evaporated to yield the hydroxy ether **4**: 39 mg (97% theoretical); identical in every respect (NMR, IR, and mass spectra and α_D) with natural decaryiol (**4**).

Acknowledgment. We express our appreciation to Professor Y. Loya and Mr. Y. Benayahu for collection and identification of the soft coral and the United States-Israel Binational Science Foundation for partial support (Grant 2201/80).

Registry No. **1**, 20489-82-1; **2**, 53915-41-6; **3**, 68042-99-9; **4**, 78039-78-8; **5**, 78087-96-4; **6**, 78039-79-9; **7**, 78087-97-5; **8**, 78039-80-2; **9**, 78039-81-3; **10**, 78039-82-4; **11**, 78039-83-5; **12**, 38746-47-3; **12** lactol (isomer 1), 78039-84-6; **12** lactol (isomer 2), 78039-85-7; **13**, 78039-86-8; α-terpinol, 10482-56-1.

Synthesis and Stereochemistry of Thiaspiro-α-methylene-γ-butyrolactones. Single-Crystal X-ray Diffraction Analysis of 2,2,6,6-Tetramethyl-9-methylene-7-oxa-1-thiaspiro[4.5]decan-8-one

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α-Methylene-γ-butyrolactone systems attached to heterocycles are rare. We reported the synthesis of a few 9-methylene-7-oxa-1-thiaspiro[4.5]decan-8-ones via a Reformatsky-type reaction on substituted 4-thianones. All products were characterized by ^1H and ^{13}C NMR analysis as well as by mass and infrared spectra and elemental analyses. Downfield shifts for C(2,6) in 2,2,6,6-tetramethyl-9-methylene-7-oxa-1-thiaspiro[4.5]decan-8-one in the ^{13}C NMR spectrum were of such magnitude, compared to model cyclohexyl systems, that the thianone ring was suggested to be flattened near the sulfur end of the molecule. The structure of solid 2,2,6,6-tetramethyl-9-methylene-7-oxa-1-thiaspiro[4.5]decan-8-one was established by means of an X-ray diffraction analysis of a single crystal and confirmed such a flattening. The molecule crystallizes in the space group $P2_1/c$ with unit cell parameters of a = 6.189 (3) Å, b = 11.244 (4) Å, c = 18.960 (9) Å, and β = 92.39 (4)°. The structure was solved by direct methods and refined by least-squares methods to an R value of 0.057 for 2515 reflections. The five-membered lactone ring is in a flattened twist (C_2) conformation, and the C-O bond has an axial orientation at the 4-position of the thiane ring system.

The diverse biological activities of the compounds having the α-methylene-γ-butyrolactone moiety have been well documented.[1] The possible utilization of these lactones as antitumor agents has attracted the attention of many

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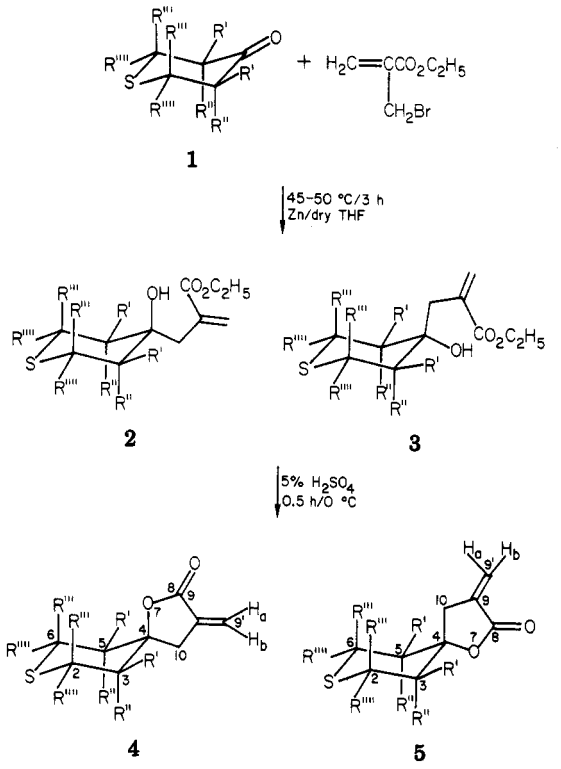
Scheme I[a]



1 2 3 4 5

[a] a, R′ = R″ = D, R‴ = R⁗ = H; b, R′ = R″ = R‴ = R⁗ = H; c, R′ = R″ = H, R‴ = R⁗ = CH_3; d, R′ = R″ = R‴ = H; R⁗ = CH_3.

workers in the field.[2] With a view for study of the anticarcinogenic properties, several carbocyclic spiro α-methylene-γ-butyrolactones were previously reported from this laboratory.[3] The influence of a heteroatom such as sulfur on the conformation of the thiane ring as well as the influence on a preference for an equatorial or axial C–O bond at the spiro juncture has not previously been fully assessed. In continuation of our search for such compounds, we had occasion to prepare several unknown thiaspiro-α-methylene-γ-butyrolactones. We now report the method of preparation and spectral studies of these compounds and a single-crystal X-ray diffraction analysis of 2,2,6,6-tetramethyl-9-methylene-7-oxa-1-thiaspiro-[4.5]decan-8-one.

Results and Discussion

Synthesis and Spectral Data. The synthesis of the spirolactones is outlined in Scheme I.[4] All compounds were obtained via a Reformatsky-type reaction. The appropriate thianone 1 was allowed to react with activated zinc[5] and ethyl α-(bromomethyl)acrylate.[6] Since the normal method of carrying out this reaction, namely, the addition of ethyl α-(bromomethyl)acrylate to a mixture of zinc and thianone, would result in the formation of sulfonium salts, a modified procedure, as given in the Experimental Section, was adopted to give intermediate 2 (or 3) leading to members of 4 (or 5). Lactones **4a–c** are conformationally related to compounds **5a–c** by a ring-reversal process. Although in solution (at room temperature) these conformers are probably in rapid reversible equilibrium, one solid with a sharp melting point was isolated in each case.

Table I. IR, ^{1}H NMR, and Mass Spectral Data for Thiaspiro-α-methylene-γ-butyrolactones

compd	IR,[d] cm^{-1}	NMR[e]
4a ⇌ 5a	1748 ($\nu_{C=O}$), 1653 ($\nu_{C=C}$)	2.42-3.07 [AB q, 4 H, H(2), H(6), J_{AB} = 14.2 Hz], 2.70 [2 H, H(10)],[a] 5.66 [1 H, H_b(9′)],[b] 6.27 [1 H, H_a(9′)][c]
4b ⇌ 5b	1748 ($\nu_{C=O}$), 1653 ($\nu_{C=C}$)	1.76-3.18 [m, 8 H, H(2), H(3), H(5), H(6)], 2.70 [2 H, H(10)],[a] 5.66 [1 H, H_b(9′)],[b] 6.27 [1 H, H_a(9′)][c]
4c ⇌ 5c	1754 ($\nu_{C=O}$), 1656 ($\nu_{C=C}$)	1.27 (s, 6 H, CH_3), 1.61 (s, 6 H, CH_3), 1.59-2.09 [AB q, 4 H, H(3), H(5), J_{AB} = 14.0 Hz], 2.72 [2 H, H(10)],[a] 5.64 [1 H, H_b(9′)],[b] 6.26 [1 H, H_a(9′)][c]
4d	1754 ($\nu_{C=O}$), 1664 ($\nu_{C=C}$)	2.04-2.41 [m, 4 H, H(3), H(5)], 2.84 [2 H, H(10)],[a] 4.54 [dd, 2 H, H(2), H(6), J = 11.0, 4.0 Hz], 5.68 [1 H, H_b(9′)],[b] 6.30 [1 H, H_a(9′)],[c] 7.20-7.50 [m, 10 H, Ar H)

[a] Three-line pattern resulting from X_2 of AMX_2 where $J_{AX} \simeq J_{MX}$ = 2.5 Hz. [b] "M" portion of AMX_2 pattern where $J_{AM} < J_{AX}$ = 2.5 Hz. The center of the triplet is taken as the peak position. [c] "A" portion of AMX_2 pattern where $J_{AM} < J_{AX} \simeq J_{MX}$ = 2.5 Hz. The center of the triplet is takn as the peak position. [d] Spectrum recorded on a KBr pellet. [e] In parts per million from Me_4Si in $DCCl_3$.

The ^{1}H NMR spectral data are reported in Table I. The signal at δ 4.54 (dd, J = 11.0, 4.0 Hz) for **4d** (or **5d**) corresponds to protons H(2) and H(6). The observed coupling constants, $^3J_{H(2a),H(3_a)} = {}^3J_{H(6_a),H(5_a)}$ = 11.0 Hz and $^3J_{H(2_a),H(3_e)} = {}^3J_{H(6_a),H(5_e)}$ = 4.0 Hz (which are typical values expected for vicinal coupling constants $^3J_{trans}$ and $^3J_{cis}$ in the chair conformation for a cyclohexane system[7]), indicate that the C(2)–H and C(6)–H bonds are axial. The signals due to the H(3) and H(5) in **4d** (or **5d**) at δ 2.04–2.41 (m, 4 H) are considerably *downfield* from the signal of similar protons in **4c** (⇌**5c**) at δ 1.59–2.09 and suggest that H(3) and H(5) in **4d** (or **5d**) are situated toward an edge of the arene ring.[8] A molecular model of **4d** suggests that H(3) and H(5) are indeed at the periphery of the benzene ring. The ^{1}H NMR spectrum of **4d** also shows that the diagmagnetic anisotropy effect of the benzene ring may be felt, although to a smaller extent, even by the distant H(10) (δ 2.84) in comparison to δ ~2.70 found for related protons in lactones **4a–c**. The assignment of the signals at δ ~5.66 and

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Table II. ^{13}C Chemical Shifts for 9-Methylene-7-oxa-1-thiaspiro[4.5]decan-8-ones[a]

compd	chemical shift							
	C(2, 6)	C(3, 5)	C(4)	C(8)	C(9)	C(9′)	C(10)	other
4a (⇌**5a**)	24.42	30.87	83.29	168.97	134.37	122.94	40.44	
4b (⇌**5b**)	24.60	38.49	80.95	169.05	134.37	122.94	40.60	
4c (⇌**5c**)	41.75	50.48	83.41	169.09	134.17	122.18	43.21	34.05 (CH_3(e)), 31.59 (CH_3(a))
4d (or **5d**)	45.28	43.97	82.54	168.93	133.93	123.33	41.51	140.17, 133.94, 128.55, 127.58, 127.29, 123.32 (Ar)

[a] In $DCCl_3$ in parts per million downfield from Me_4Si.

Table III. ^{13}C Chemical Shifts for 3-Methylene-1-oxaspiro[4.5]decan-2-ones[a]

compd	chemical shifts								
	C(2)	C(3)	C(3′)	C(4)	C(5)	C(6), C(10)	C(7), C(9)	C(8)	other
6a (⇌**7a**)	169.52	135.52	121.83	39.52	83.21	37.42	22.50	24.76	
6b	169.64	135.48	121.71	40.64	82.34	38.10	22.94	46.98	32.34 ($C(CH_3)_3$) 27.50 ($C(CH_3)_3$)
7b	166.35	135.48	121.91	37.30	83.97	37.42	24.05	46.63	32.18 ($C(CH_3)_3$), 27.50 ($C(CH_3)_3$)
6c (⇌**7c**)	169.52	135.48	121.47	41.39	83.49	49.44, 37.42	31.31, 18.93	38.18	31.71 (CH_3(e)), 28.21 (CH_3(a))
6d (⇌**7d**)	169.52	135.12	121.15	42.78	84.09	49.09	31.55	51.11	35.16 (CH_3(e)), 28.65 (CH_3(a))

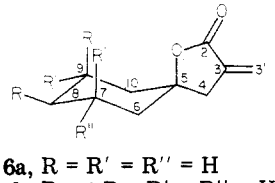
[a] In $DCCl_3$, in parts per million downfield from $(CH_3)_4Si$.

6.27 for $H_b(9')$ and $H_a(9')$, respectively, was made on the basis of the empirical correlation (eq 1) developed by

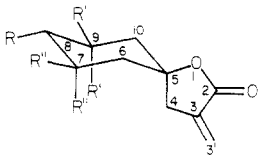
$$\delta = 5.28 + Z_{gem} + Z_{cis} + Z_{trans} \quad (1)$$

Tobey[9] and Pascual, Meier, and Simon[10] for the chemical shift of a proton on a double bond. Thus the calculated values of $\delta_{H_a(9')}$ 6.14 and $\delta_{H_b(9')}$ 5.58 compare favorably with the experimental values (Table I).

The ^{13}C NMR spectral data for 9-methylene-7-oxa-1-thiaspiro[4.5]decan-8-ones are recorded in Table II and are compared with the ^{13}C chemical shifts of 3-methylene-1-oxaspiro[4.5]decan-2-ones[11] **6a–d** or **7a–d** given in Table III. The electrostatic effect on α-carbons due to the incorporation of a sulfur atom in the ring could be gleaned by a simple comparison of the chemical shifts for C(2) and C(6) in **4b** (⇌**5b**) and **4c** (⇌**5c**) with those for C(7) and C(9) in **6a** (⇌**7a**) and **6d** (⇌**7d**). The presence of the



6a, R = R′ = R″ = H
b, R = *t*-Bu; R′ = R″ = H
c, R = R′ = H; R″ = CH_3
d, R = H; R′ = R″ = CH_3



7a, R = R′ = R″ = H
b, R = *t*-Bu; R′ = R″ = H
c, R = R′ = H; R″ = CH_3
d, R = H; R′ = R″ = CH_3

sulfur atom in **4b** (⇌**5b**) and **4c** (⇌**5c**) causes a downfield shift for C(2) and C(6) compared with the shifts for C(7) and C(9) in **6a** (⇌**7a**) and **6d** (⇌**7d**). Likewise, a deshielding effect for β-carbons as exerted by the sulfur atom was also noteworthy in compounds **4b** (⇌**5b**) and **4c** (⇌**5c**). An upfield γ shift was observed for the resonances of C(4) in **4b** (⇌**5b**) and **4c** (⇌**5c**) relative to the comparable signals in **6a** (⇌**7a**) and **6d** (⇌**7d**). Similar effects were observed in the case of substituted 4-thianones[12a] and thianes.[12b] The origin of the upfield γ shift is not clearly known, but arguments have been presented for a field effect[13,14] as well as for a hyperconjugative-type interaction of an electron pair on a heteroatom through the Cα–Cβ bond affecting the shift of the antiperiplanar γ-carbon atom.[15]

Table IV. ^{13}C Chemical Shift Data for Selected Carbons in Thianes[a] and Cyclohexanes[b]

compd	chemical shift	
	C(2, 6)	C(3, 5)
8a[32]	29.06	27.76
8b	41.61	40.97
8c[33]	49.07	34.17
9a[34]	27.7	27.7
9b[34]	28.2	27.8

[a] In $DCCl_3$ from Me_4Si. [b] In parts per million from Me_4Si.[34,35]

The dependence of shielding of the carbinyl carbon upon the configuration of an attached hydroxyl group has been clearly established in the case of alicyclic alcohols[16] and 1-hetera-4-cyclohexanols,[12] an axial hydroxyl group shielding the attached carbon by about 5 ppm compared to the equatorial counterpart. The axial C–O bond shields the spiro carbon in *cis*-6-*tert*-butyl-1-oxaspiro[2.5]octane

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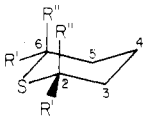
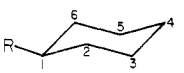
by 1.5 ppm, compared with the equatorial C–O bond in its epimer.[17] Similarly, in *cis*-8-*tert*-butyl-3-methylene-1-oxaspiro[4.5]decan-2-one (**6b**), C(5) is shielded by 1.63 ppm in comparison to its counterpart in the trans isomer **7b** (Table III).

Lactones **4d** and **5d** are configurational isomers and are not interconvertible by a ring reversal process. Unfortunately, under the reaction conditions only one isomer **4d** could be isolated. The preferential formation of *cis*-8-*tert*-butyl-3-methylene-1-oxaspiro[4.5]decan-2-one rather than the trans isomer has been reported.[3b] From this fact and the ^{1}H NMR data as well as our observation of the preferential crystallization of **4c** (as evidenced by the X-ray diffraction analysis given later in the paper), we tentatively assign the C(4)–O(7) bond as axial in 2,6-diphenyl-9-methylene-7-oxa-1-thiaspiro[4,5]decan-8-one (**4d**).

Interesting effects of the spirolactone moiety on the C(2,6) and C(3,5) ^{13}C chemical shifts in **8** and **9** were found



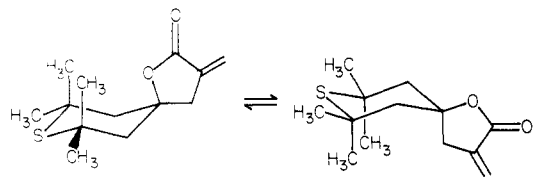
8a, R′ = R″ = H
b, R′ = R″ = CH_3
c, R′ = C_6H_5; R″ = H



9a, R = H
b, R = $C(CH_3)_3$

(see Tables II–IV). Thianes **8b** and **8c** were obtained by a reduction of the corresponding thianones **1c**[18,19] and **1d**.[20] A downfield shift (9–10 ppm) for C(3) and C(5) in **4b** (⇌**5b**), **4c** (⇌**5c**), and **4d** was found in comparison with the corresponding carbons in **8a–c**, respectively. Upfield shifts of 4.46 and 3.79 ppm for C(2) and C(6) were found in **4b** (⇌**5b**) and **4d** which may presumably be due to the γ_a effect of the axial C–O or C–CH_2 bond.[12b] Similar downfield shifts for C(6,10) and upfield shifts for C(7,9) were also observed in the case of **6a** (⇌**7a**), **6b**, and **7b** in comparison with the corresponding carbons in **9a** and **9b**. Such effects have been noted in substituted alicyclic[16] and heterocyclic[12] alcohols. The γ_a effect is not felt by C(2) and C(6) in **4c** (⇌**5c**). This is probably due to *significant flattening* of the thiane ring at the sulfur end which could alleviate the 1,3-diaxial interaction between the axial methyl groups and the axial C–O or C–CH_2 bond (see X-ray evidence given below).

In solution, 2,2,6,6-tetramethyl-9-methylene-7-oxa-1-thiaspiro[4,5]decan-8-one presumably exists as an equilibrium mixture of **4c** and **5c**. Isolation of one conformer

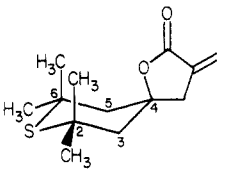


4c ⇌ **5c**

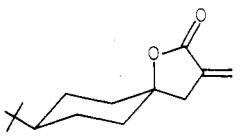
as a crystalline solid suggests that it was the conformer with lower lattice packing energy. Although the preference for an axial C–O bond over an equatorial C–O bond has been illustrated in 3-methylene-1-oxaspiro[4,5]decan-2-one,[3b] by preferential crystallization of either **4c** or **5c** could not be predicted on the basis of the steric requirements of the axial methyl groups at C(2) and C(6). In order to establish the conformation of this compound in an unequivocal fashion, we performed an X-ray diffraction analysis on a single crystal of 2,2,6,6-tetramethyl-9-methylene-7-oxa-1-thiaspiro[4,5]decan-8-one (**4c**).

Single-Crystal Analysis. A stereoview of the compound **4c** is shown in Figure 1. Bond distances (Figure 2), bond angles (Figure 3), torsion angles for the two ring systems (Figure 4), positional parameters for the nonhydrogen atoms, and positional parameters for the hydrogen atoms are available as supplementary material.

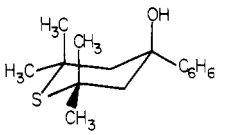
The structure consists of a six-membered thiane ring in the chair conformation with a spiro-fused, α-methylene-substituted γ-lactone at the 4-position and two methyl groups each attached to the carbons at the 2- and 6-positions. The oxygen attached to the spiro carbon atom is in an axial position with respect to the six-membered ring. The structure can most easily be compared to *cis*-8-*tert*-butyl-3-methylene-1-oxaspiro[4,5]decan-2-one (**6b**)[3b] and to 2,2,6,6-tetramethyl-4(e)-phenylthian-4(a)-ol (**10**).[21]



4c



6b



10

Overall, the conformation of the six-membered ring in **4c** more closely resembles the conformation of **10** than of **6b**. In both **4c** and **10**, the thiane ring is significantly flattened at the sulfur position in comparison to both cyclohexane and **6b**. The endocyclic torsion angles around the S(1)–C(2) and S(1)–C(6) bonds of **4c** have an average magnitude of 47.0° compared to 45.8° in **10**. This is 10° less than the ideal value of 57° for cyclohexane and 12.9° less than the average of 59.9° for the corresponding C–C bonds in **6b**. Both **4c** and **10** are also significantly flattened in comparison to other thiane structures.[22] The flattening can be accounted for by the steric interactions between the lone-pair electrons of the sulfur atom and the bulky methyl groups attached to C(2) and C(6). There are a number of sulfur–hydrogen intramolecular contacts which are less than the expected van der Waals distance of 3.00 Å: on one side of the ring, S(1)–H(11B) = 2.97 Å, and S(1)–H(13B) = 2.91 Å; on the opposite side, S(1)–H(3A) = 2.88 Å, S(1)–H(5B) = 2.99 Å, S(1)–H(12A) = 2.68 Å, S(1)–H(12C) = 2.81 Å, S(1)–H(14A) = 2.79 Å, and S(1)–H(14C) = 2.83 Å. (The A–C designations are for the hydrogen atoms attached to the methyl carbon atoms.) Associated with the flattening of the ring is a widening of the C(2)–S(1)–C(6) angle to 105.3 (1)°. This is larger than those found in a number of other thiane structures (range 98.7–99.8°)[21,22] but parallels the value of 105.62 (5)° seen in **10**. Strain is also relieved by an increase of the endocyclic bond angles at C(3) and C(5).

In comparison with **6b**, the six-membered ring of **4c** is much less flattened around the spiro carbon atom. The average endocyclic torsion angle around the C(3)–C(4) and

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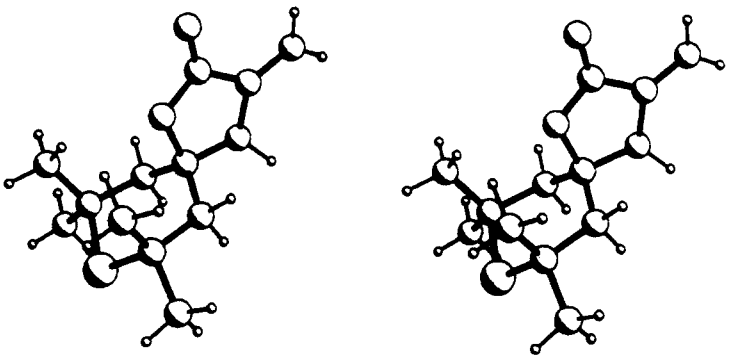

Figure 1. PLUTO[30] drawing of a single molecule of 2,2,6,6-tetramethyl-9-methylene-7-oxa-1-thiaspiro[4.5]decan-8-one (**4c**).

C(4)–C(5) bonds is 52.9° compared to an average of only 49.2° in **6b**. The result is a balance between a number of short intramolecular distances between O(7) and the axial methyl groups on one side of the ring and between the hydrogens attached to C(3), C(5), and C(10) on the opposite side of the ring. For the oxygen atom, close contacts occur as follows: O(7)–H(11A) = 2.45 Å and O(7)–H(13A) = 2.43 Å. On the other side of the ring the close contacts are H(10A)–H(5A)(e) = 2.50 Å, H(10A)–H(5B)(a) = 2.37 Å, H(10B)–H(3B)(e) = 2.52 Å, and H(10B)–H(3A)(a) = 2.53 Å.

The carbon–sulfur bonds [average 1.833 (2) Å] are slightly longer than the value of 1.817 (5) Å given by Sutton as the mean distance for paraffinic C–S bonds,[23] but are within the range (1.811–1.840 Å) found in several cyclic thianes previously reported.[21,22]

As in **6b**, the five-membered lactone ring is in a flattened twist (C_2) conformation as indicated by the internal torsion angles shown in Figure 4 and by the calculation of the pseudorotation parameter, Δ.[24] Compared to an ideal twist conformation in cyclopentane (Δ = 0.0°) and the ideal envelope conformation (Δ = 36.0°),[25] the value of Δ for **4c** is 0.8°. The approximate 2-fold axis passes through the atoms O(15) and C(18) and bisects the C(4)–C(10) bond. The ring is much flatter in **4c** than in **6b**. Table VII (supplementary material) gives the perpendicular atoms of the lactone ring. As shown in the table, the atoms C(4), O(7), C(9), O(10), and C(16) are all significantly further from the plane in **6b** than in **4c**. The average distance of all the atoms listed from the plane is only 0.05 Å for **4c** compared to 0.11 Å in **6b**.

Bond distances in the lactone ring compare very well with those of **6b** and with the values of several natural products containing methylene substituted γ-lactone rings.[25-29] The largest differences between **4c** and **6b** are for O(7)–C(8) and C(4)–C(10) (0.016 Å). The remaining bonds differ by less than 0.01 Å. Similar small differences exist between **4c** and the lactone rings of the natural products. Likewise, bond angles in the lactone rings of **4c** and **6b** only differ in the range of 0.3–1.7°, with the largest difference being between the C(4)–O(7)–C(8) angles (110.8° in **6b**).

There are only a few short intermolecular nonbonded distances: H(10B)–O(15) = 2.44 Å [O(15) transformed by $x - 1, y, z$] and H(13C)–S(1) = 2.93 Å [S(1) transformed by $1 - x, {}^1/_2 + y, {}^1/_2 - z$]. The shortest hydrogen–hydrogen intermolecular distance was 2.33 Å, with only two other such distances less than 2.4 Å.

Thus, the data confirm the conformation for **4c** as having a flattened 4-thiane structure as predicted from ^{13}C NMR analysis. This may well be due to the interactions of the methyl groups at C(2,6) and the pairs of nonbonding electrons on the sulfur atom.

Experimental Section

Melting points were obtained on a Thomas-Hoover melting point apparatus and are uncorrected. The ^1H NMR spectra and broad-band proton-decoupled ^{13}C NMR spectra were obtained on a Varian XL-100(15) NMR spectrometer equipped with a Nicolet TT-100 PFT accessory operating at 100.1 MHz for ^1H observation and at 25.2 MHz for ^{13}C signals with tetramethylsilane as the internal standard. IR spectra were recorded on a Beckmann IR-5A unit. Mass spectral data were collected on a CEC Model 21-110B HR mass spectrometer. Elemental analysis were performed by Galbraith Laboratories.

General Procedure for the Synthesis of the 9-Methylene-7-oxa-1-thiaspiro[4.5]decan-8-ones. In a three-necked, 50-mL, round-bottomed flask, equipped with a magnetic stirrer, condenser, two pressure-equalizing addition funnels, and a N_2 inlet, was placed activated zinc[5] (20 mesh, 0.72 g, 0.011 mol). The appropriate thianone (0.01 mol) in 10 mL of dry THF and ethyl α-(bromomethyl)acrylate[6] (0.01 mol) in 10 mL of dry THF were introduced separately into the two addition funnels. Twenty-five drops of the solution of the ester were first added to the activated zinc, keeping the temperature at 45–50 °C. After 3 min, during which time the Reformatsky reagent was formed, twenty-five drops of the solution of thianone were added. This was followed by the addition, after 3 min, of twenty-five drops of the solution of ester. After these alternate additions were completed (ca. 2 h, the temperature being maintained at 45–50 °C during the entire period), the reaction mixture was stirred for an additional period of 3 h at 45–50 °C. This new reaction mixture was then added to 100 mL of ice-cold 5% H_2SO_4. This usually yielded an oily product. Extraction with portions of ether (3 × 50 mL), drying (Na_2SO_4) the combined ether extracts, and removal of ether by rotary evaporation resulted in the formation of an oil or a crystalline product which was recrystallized from suitable solvents.

Purification of 9-Methylene-7-oxa-1-thiaspiro[4.5]decan-8-one (4b ⇌ 5b). The product resulting from the above reaction using 4-thianone (**1b**; Aldrich Chemical Co., Inc.) as the general ketone was isolated from the ether solution as a viscous oil. The oil was dissolved in 2 mL of absolute methanol, and the solution was cooled to −78 °C. A solid form was quickly filtered and recrystallized (absolute CH_3OH) to afford 0.26 g (14.2%) of **4b** (⇌**5b**), mp 94–95 °C. Anal. Calcd for $C_9H_{12}O_2S$: C, 58.65; H, 6.58; S, 17.41. Found: C, 58.59; H, 6.63; S, 17.45.

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Table V. Summary of Crystallographic Data for 2,2,6,6-Tetramethyl-9-methylene-7-oxa-1-thiaspiro[4.5]decan-8-one (4c)

molecule	$C_{13}H_{20}O_2S$
mol wt	240.4 g/mol
linear abs coeff	19.4 cm^{-1} ($CuK\bar{\alpha}$)
calcd density	1.221 g/cm^3
space group	$P2_1/c$
cell dimensions (138 ± 2 K)	a = 6.189 (3) Å
	b = 11.244 (4)
	c = 18.960 (9)
	$\alpha = \gamma = 90.0°$
	β = 92.39 (4)°
	V = 1318 $Å^3$
	Z = 4
crystal size	(1) 0.5 × 0.2 × 0.2 mm
	(2) 0.24 × 0.26 × 0.04 mm
no. of rflctns measd	2515
obsd ($F > 5\sigma(F)$)	2370
final R, all rflctns	0.057
R_w, all rflctns	0.077

Preparation of 9-Methylene-7-oxa-1-thiaspiro[4.5]decan-8-one-*3,3,5,5-d*$_4$ (4a ⇌ 5a). The reaction of 4-thianone-*3,3,5,5-d*$_4$[18] (1a; 1.20 g, 0.01 mol) with Zn (0.72 g, 0.011 mol) and ethyl α-(bromomethyl)acrylate (1.93 g, 0.01 mol) in the manner described for the undeuterated thianone **4b** yielded, after recrystallization (absolute CH_3OH), 0.286 g (15.2%) of spirolactone **4a** (⇌**5a**), mp 94–96 °C. Anal. Calcd for $C_9H_{12}O_2S$: m/e 188.0809. Found m/e 188.0807.

Purification of 2,2,6,6-Tetramethyl-9-methylene-7-oxa-1-thiaspiro[4.5]decan-8-one (4c ⇌ 5c). 2,2,6,6-Tetramethyl-4-thianone (1c) was prepared by the method of Noyler.[19] This ketone was allowed to react with the Reformatsky reagent as described in the general procedure. The product was isolated as an oil from the ether extract and crystallized upon being allowed to stand under refrigeration. Recrystallization [1:1 methanol–petroleum ether (bp 60–80 °C)] afforded 0.817 g (34%) of lactone **4c** (⇌**5c**), mp 109–111 °C. Anal. Calcd for $C_{13}H_{20}O_2S$: C, 64.95; 8.39; S, 13.34. Found: C, 64.88; H, 8.41; S, 13.27.

Synthesis of 2,6-Diphenyl-9-methylene-7-oxa-1-thiaspiro[4.5]decan-8-one (4d). The product from inclusion of *r*-2,*cis*-6-diphenyl-4-thianone[20] (1d) in the reaction described above (for **4h**) was isolated as a crystalline material from the ether extract. The crude product was recrystallized twice [1:1 methanol–hexane (20 mL) containing a little (0.5 mL) benzene] to yield 0.336 g (10%) of **4d**, mp 148.5–149.5 °C. Anal. Calcd for $C_{21}H_{20}O_2S$: C, 75.00; H, 5.95; S, 9.54. Found: C, 75.08; H, 6.03; S, 9.72.

Preparation of 2,2,6,6-Tetramethylthiane (8b). To a solution of 2,2,6,6-tetramethyl-4-thianone[19] (1c; 0.9 g, 5.23 mmol) and hydrazine (90%, 1 mL) in diethylene glycol (10 mL) was added potassium hydroxide pellets (1.0 g, 17.86 mmol). The mixture was warmed to dissolve the KOH and then stirred at 170–175 °C (oil bath) under N_2 for 5 h. The reaction mixture was cooled to room temperature, poured into water (100 mL), and extracted with ether (3 × 15 mL). The combined ethereal layer was washed with water (2 × 15 mL) and dried ($MgSO_4$). Removal of ether and distillation of the residue gave pure 2,2,6,6-tetramethylthiane (**8b**) as a colorless oil: 0.70 g (84,7%); bp 44–45 °C (12 mm); IR (neat) showed the absence of a carbonyl band; ^1H NMR ($DCCl_3$) δ 1.32 (s, 12 H, 4-CH_3), 1.56–1.74 [m, 6 H, H(3), H(4), H(5)]; ^{13}C NMR ($DCCl_3$) δ 41.61 [C(2), C(6)], 40.97 [C(3), C(5)], 31.92 (CH_3), 19.64 [C(4)]. Anal. Calcd for $C_9H_{18}S$: m/e 158.1129. Found: m/e 158.1134.

Crystallographic Experimental Data. Ketone **4c** was found to crystallize in two forms, depending on the solvent system. When recrystallized by slow evaporation from methanol, the crystals were monoclinic, but when crystallized from petroleum ether or methanol in equilibrium with petroleum ether, the crystals were orthorhombic. Both types were rather flat plates although the monoclinic crystals were slightly more needlelike in shape. The data crystals were in the monoclinic space group $P2_1/c$. The unit cell dimensions (see Table V) and intensity data were obtained with an Enraf-Nonius CAD-4 diffractometer fitted with a low-temperature apparatus.

The cell parameters were obtained by a least-squares fit to the $+2\theta$ and -2θ values of 36 reflections at 138 ± 2 K by using Cu $K\alpha_1$ (λ = 1.5405 Å) radiation. The intensity data for all reflections with $4° \leq 2\theta \leq 150°$ were measured using Cu $K\bar{\alpha}$ radiation (λ = 1.541 78 Å) and the θ–2θ scan technique. Two different crystals were used for data collection; the first, larger crystal was used to collect data for l = 0–9 and the second, smaller one for l = 9–11. The angular scan width was variable and taken to be (1.54 + 0.14 tan θ)° for the first crystal and (0.80 + 0.15 tan θ)° for the second. A receiving aperture with a variable width of (1.5 + 0.5 tan θ) mm for the first crystal and (3.5 + 0.86 tan θ) mm for the second and a constant height of 6 mm was located at a distance of 173 mm from the crystal. The maximum scan time was 150 s for the first crystal and 75 s for the second crystal. For each reflection two-thirds of the scan time was spent scanning the peak, and one-sixth was spent scanning each of the two backgrounds. During the intensity measurements, the intensities of three standard reflections were monitored after every 6000 s of X-ray exposure time for the first crystal and every 4000 s for the second crystal and indicated no appreciable decomposition of the crystal. A total of 2515 unique reflections were measured of which 285 were considered unobserved, having observed structure factors less than $5\sigma(F_0)$. All intensity data were corrected for Lorentz and polarization factors.

Structure Determination and Refinement. The structure was determined by direct methods with the program SHELX.[31] The phases of 392 reflections having a normalized structure factor (E) greater than 1.2 were used to construct E maps. The map with second highest reliability factor (parachor = 1.694) gave 15 of the 16 atoms in the structure among the top 22 peaks. The map with the highest reliability factor (parachor = 2.664) gave 13 reasonable peaks, but the structure could not be refined. After isotropic refinement of the nonhydrogen atoms found in the second E map, the remaining atom of the structure was located in a difference map.

The nonhydrogen atoms were refined by least-squares methods in stages with isotropic and anisotropic thermal parameters. Difference maps were used to locate the hydrogen atoms which were then refined isotropically.

The least-squares refinements were carried out by a full-matrix method with the computer program SHELX. The scattering factors were taken from the literature.[36] The weighting scheme used was as shown in eq 2 with σ_F defined as shown in eq 3 and where

$$W_F = K/(\sigma_F^2 + gF^2) \tag{2}$$

$$\sigma_F = 0.5[(\sigma^2 + (0.04P)^2)/P\mathrm{Lp}]^{1/2} \tag{3}$$

$\sigma = T^{1/2}\upsilon$, υ = scan speed, T = pK + 4(R + L), P = [Pk – 2(R + L)]υ, Pk = peak height, R = right background, L = left background, and Lp = Lorentz and polarization correction. The factors K and g were redetermined after each structure factor calculation and had the values 0.1451 and 0.0222, respectively, after the final cycle of refinement.

The variance was calculated as shown in eq 4, where N is the

$$\upsilon = [M\Sigma[W_F(|F_o| - |F_c|)^2]/N\Sigma W_F]^{1/2} \tag{4}$$

number of reflections in a group, M is the total number of reflections, the sum in the numerator is over all the reflections in a group, and the sum in the denominator is over all the reflections. An analysis of the variance in terms of the parity of the reflection indices, sin θ, and $(F_o/F_{max})^{1/2}$ showed no significant variation of

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v for various ranges of the functions tested. Refinement was terminated when all parameter shifts were less than 0.10 of their corresponding standard deviations. The final value of R for all 2515 reflections was 0.057 and that for R_w, where $R_w = \sum W_F^{1/2}[F_o - F_c]/\sum W_F^{1/2}|F_o|$, was 0.077.

Acknowledgment. Grateful acknowledgment is given to the National Institutes of Health of the USPHS for a grant from the National Cancer Institute (Grant No. CA 22770-03 to K.D.B. and Grant No. CA 17562 to D.v.d.H.) for partial support of this research.

Registry No. **1a**, 22842-37-1; **1b**, 1072-72-6; **1c**, 22842-41-7; **1d**, 18456-44-5; **4a**, 73321-76-3; **4b**, 73321-78-5; **4c**, 73321-77-4; **4d**, 78804-16-7; **6a**, 52978-85-5; **6b**, 67464-47-5; **6c**, 67464-48-6; **6d**, 67464-49-7; 7b, 67464-50-0; **8b**, 78050-22-3; ethyl α-(bromomethyl)-acrylate, 17435-72-2.

Supplementary Material Available: Figures 2–4 and tables containing positional parameters for nonhydrogen atoms, anisotropic thermal parameters, hydrogen positional, thermal parameters, and a listing of observed and calculated structure factor amplitudes for **4c** (14 pages). Ordering information is given on any current masthead page.

Notes

Synthesis of 5,5-Dichloro-4-pentenoic Acid by the Wittig Reaction with Bromotrichloromethane and Triphenylphosphine

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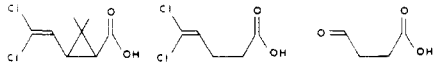
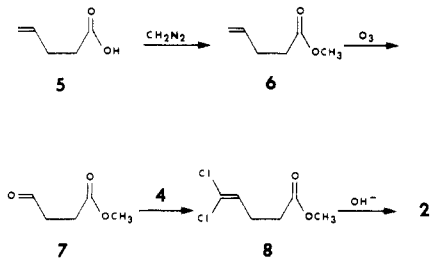
In 1973, Elliott et al.[1] described the insecticidal properties of permethrin, an important synthetic pyrethroid derived from 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylic acid (**1**). In subsequent studies on the acid moiety of these insecticides, a number of investigators have shown that the intact cyclopropane ring was an unnecessary structural feature for high activity.[2] For example, the cyano(3-phenoxyphenyl)methyl ester of (±)-4-chloro-α-(1-methylethyl)benzeneacetic acid, commonly known as fenvalerate, has reached the commercial stage of development. Despite these facts, few published reports have dealt specifically with analogues of **1** in which the cyclopropane ring system was absent. At the onset of this work, it was decided that 5,5-dichloro-4-pentenoic acid (**2**) would serve as a useful intermediate for structure–activity studies on synthetic pyrethroid insecticides. To my knowledge, **2** has not been described in the recent literature, but a series of insecticidally active esters of this acid, with substituents at the α (C-2) position, have recently been patented.[3] These patents have encouraged the publication of the chemistry that has been explored during the synthesis of **2**.



1 **2** **3**

On the assumption that the dichloromethylene group (=CCl_2) could be introduced into 4-oxobutanoic acid (**3**)[4] by the Wittig reaction with (dichloromethylene)triphenylphosphorane (**4**), now prepared to advantage by the interaction of $CBrCl_3$ with Ph_3P (eq 1)[5] rather than CCl_4 with Ph_3P,[6] then the synthesis of **2** appeared to be a straightforward task, at least by comparison to the synthesis of **1** by similar approaches.[7] In this work, **2** was obtained by use of the Wittig reaction, when **4** was generated according to eq 1.

Scheme I



5 **6** **7** **8**

$$2Ph_3P + CBrCl_3 \rightarrow \underset{\mathbf{4}}{Ph_3P{=}CCl_2} + Ph_3PBrCl \quad (1)$$

4-Pentenoic acid (**5**) was the preferred starting material for the synthesis of **2** (Scheme I). Ozonolysis of methyl ester (**6**) in methylene chloride solution at −78 °C gave the desired ester aldehyde, methyl 4-oxobutanoate (**7**).[8] Either Ph_3P[9] or Me_2S[10] was employed as reducing agent, allowing the isolation of pure **7** in yields of 45–60%. The properties of distilled samples of **7** agreed with those reported in the literature.[11]

The Wittig reaction on **7**, performed by allowing the aldehyde to interact with a mixture of $CBrCl_3$ and Ph_3P

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(8) For related ozonolyses, see: (a) P. L. Stotter and J. B. Eppner, *Tetrahedron Lett.*, 2417 (1973); (b) H. Zamarlik, *C. R. Acad. Sci., Ser. C*, 1138 (1970).

(9) W. G. Taylor, *J. Org. Chem.*, **44**, 1020 (1979).

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(11) H. Sumitoto, K. Kobayashi, and T. Saji, *J. Polym. Sci., Polym. Chem. Ed.*, **10**, 3421 (1972).

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