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Preparation and Stereochemistry of Some Substituted 4-Thianones and 4-Thianols. Single-Crystal Analysis of *r*-2,*trans*-6-Diphenyl-*cis*-3-methyl-4-thianone and *r*-2,*trans*-6-Diphenyl-*cis*-3-ethyl-4-thianone

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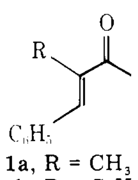
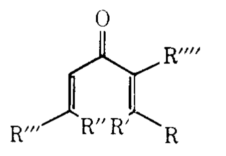
A number of substituted 4-thianones and 4-thianols have been prepared. Methods of formation, IR, ^{1}H NMR, and ^{13}C NMR analysis indicated the conformation of the heterocyclic ring in the cases studied to be predominantly of the chair form. The structures of *r*-2,*trans*-6-diphenyl-*cis*-3-methyl- and *r*-2,*trans*-6-diphenyl-*cis*-3-ethyl-4-thianone were determined by single-crystal X-ray diffraction studies. The space group for the two compounds is *Iba*2, with unit cell dimensions of a = 39.389, b = 10.5224, and c = 7.1062 Å for the methyl derivative and a = 39.414, b = 10.8315, and c = 7.3941 Å for the ethyl derivative. The structures were solved from diffractometer data and refined to $R-$ values of 0.060 and 0.058, respectively.

Simple six-membered sulfur heterocyclics are known to exist mostly in the chair conformation.[1-8] In contrast, a few six-membered nitrogen heterocyclics with a preferred boat conformation are recorded. For example, pseudotropine,[9] phenyl 3α-phenyl-3β-tropanyl ketone,[10] and 1,2,2,6,6-pentamethyl-4-phenyl-4-piperidinol[11] have been reported to exist in the boat form. In connection with a study on ^{13}C NMR spectra of some substituted thiane derivatives, we had an occasion to prepare a number of substituted 4-thianones and 4-thianols and certain derivatives thereof. We now report the methods of preparation and present evidence for the configuration and conformation of the saturated sulfur heterocycles. The first single-crystal analysis of a substituted 4-thianone is also recorded.



1a, R = CH_3
b, R = C_2H_5



2a, R′ = R″ = R″″ = H; R = R‴ = C_6H_5
b, R′ = R″ = R″″ = H; R = R‴ = $C_6H_4OCH_3$-*p*
c, R′ = R″ = H; R = R‴ = C_6H_5; R″″ = CH_3
d, R′ = R″ = H; R = R‴ = C_6H_5; R″″ = C_2H_5
e, R = C_6H_5; R′ = H; R″ = R‴ = CH_3; R″″ = H

Results and Discussion

The preparation of 2,6-diphenyl-4-thianone was first reported by Arndt and co-workers.[12] The reaction of dibenzalacetone with H_2S in the presence of sodium acetate leads to the formation of both *cis*- and *trans*-2,6-diphenyl-4-thianone. Although this method gives good yields, it is limited by the number of appropriate precursors available, such as **1** and **2**. In the present investigation, the unsymmetrical distyryl ketones **2c** and **2d** were prepared by the condensation of mononobenzilidine derivatives **1a** and **1b** with benzaldehyde in the presence of aqueous sodium hydroxide under controlled conditions. Incidentally, the reaction of benzaldehyde and methyl ethyl ketone with concentrated hydrochloric acid has been reported by Metayer[13] to furnish **2d** as a side product.

$$\mathbf{1a}\ (\text{or } \mathbf{1b}) \xrightarrow[2.\ C_6H_5CHO]{1.\ NaOH/H_2O} \mathbf{2c}\ (\text{or } \mathbf{2d})$$

In our hands, reaction of unsymmetrical 1,4-pentadien-3-one (**2c**) with H_2S in the presence of sodium acetate or Triton B led to the formation of both *r*-2,*cis*-6-diphenyl-*trans*-3-methyl-4-thianone (**3c**) and *r*-2,*trans*-6-diphenyl-*cis*-3-methyl-4-thianone (**4b**), but under different *conditions*. Higher ratio of base/dienone concentration, lower temperature, and shorter reaction time favored the formation of thermodynamically less stable **4b**. If the concentration of the sodium acetate was *decreased* and the temperature of the reaction and the heating time were both increased, the **3c** predominated. The syntheses for **3a–e** and **4a–c** were similar, and details are in the Experimental Section.

Stereochemistry of the 4-Thianones. If the chair conformation is assumed for the heterocyclic ring, the two aryl groups and the methyl group in **3c** or the ethyl group in **3d**

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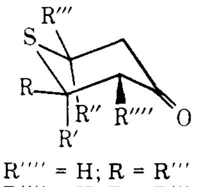
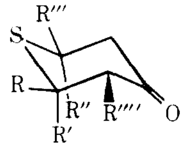
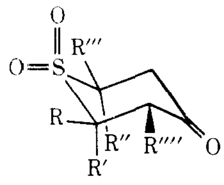


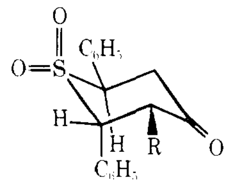
3a, R′ = R″ = R⁗ = H; R = R‴ = C_6H_5
b, R′ = R″ = R⁗ = H; R = R‴ = p-$CH_3OC_6H_4$
c, R′ = R″ = H; R = R‴ = C_6H_5; R⁗ = CH_3
d, R′ = R″ = H; R = R‴ = C_6H_5; R⁗ = C_2H_5
e, R = C_6H_5; R′ = R⁗ = H; R″ = R‴ = CH_3



4a, R = R″ = R⁗ = H; R′ = R‴ = C_6H_5
b, R = R″ = H; R′ = R‴ = C_6H_5; R⁗ = CH_3
c, R = R″ = H; R′ = R‴ = C_6H_5; R⁗ = C_2H_5



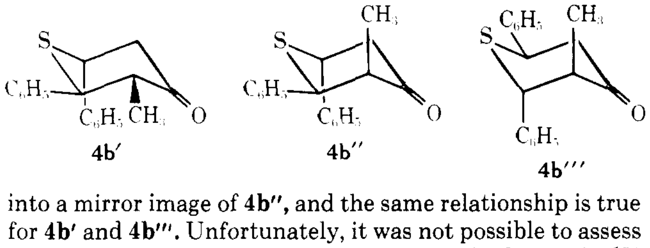
5a, R′ = R″ = H; R = R‴ = C_6H_5; R⁗ = CH_3
b, R′ = R″ = H; R = R‴ = C_6H_5; R′ ″ = C_2H_5



6a, R = CH_3
b, R = C_2H_5

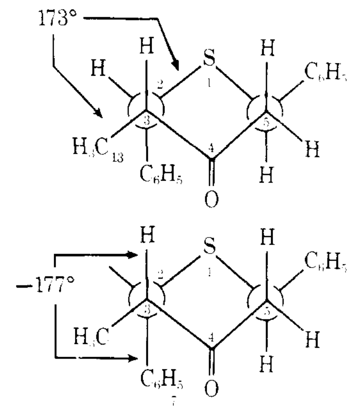
might be expected to occupy more stable equatorial positions. This seems reasonable in view of the conditions used in the synthesis. Detailed information regarding the configuration (since **3c** and **3d** have syn-arranged phenyl groups, we have labeled them as cis compounds) of thianones **3c** and **3d** can be gleaned by analysis of the ^1H NMR spectrum. The signals at δ 3.90 (d, J = 11.5 Hz) and 4.24 (dd, J = 11.5 and 3.5 Hz) for **3c** correspond to protons bonded to C(2) and C(6), respectively. The observed large coupling constant $J_{H(2a),H(3a)}$ = 11.5 Hz certainly suggests that the phenyl group and methyl group are in equatorial positions. The coupling constants $J_{H(6a),H(5a)}$ and $J_{H(6a),H(5e)}$ (11.5 and 3.5 Hz), which are typical for vicinal coupling constants J_{anti} and J_{gauche} in the chair conformation,[14] indicate that the proton at C(6) is in the axial position. The ^1H NMR spectra of protons bonded to C(2) and C(6) in **3c** and **3d** are quite similar, indicating that the two derivatives probably have the same conformation.

However, three additional structures **4b′**–**4b‴** should be considered for trans isomer **4b**. Ring reversal can convert **4b**

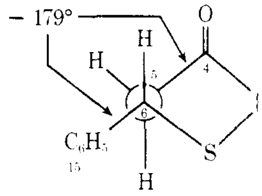


4b′ **4b″** **4b‴**

into a mirror image of **4b″**, and the same relationship is true for **4b′** and **4b‴**. Unfortunately, it was not possible to assess the relative stereochemistry of the compounds **4b** or **4c** by ^1H NMR analysis. It has been reported that *trans*-2,6-diphenyl-4-thianone (**4a**) exists in a nonchair conformation, based on dipole moment data.[15] Although the assignment may be correct, it seemed that X-ray analysis of a crystal of a member of this family would permit possible correlations with other related systems in an unequivocal fashion. Thus, we have obtained X-ray diffraction data on single crystals of **4b** and **4c**; the data are given later in this paper. To the best of our knowledge, these data are the first for 4-thianones.[16] Examination of the torsional angles S(1)–C(2)–C(3)–C(13) and C(7)–C(2)–C(3)–H(3) for **4b** (or **4c**) confirms that the methyl (or ethyl) group occupies an equatorial position and the phenyl group at C(2) is axial. The value of torsional angle C(4)–C(5)–C(6)–C(15) is proof for the equatorial C_6H_5–C(6)

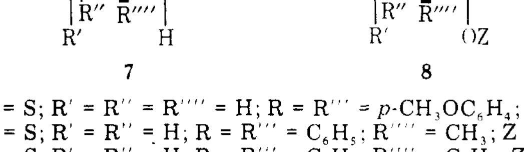


bond. Hence, the structure of the methyl-substituted isomer is **4b**. In each case, the phenyl at C(2) is axially disposed while the methyl or ethyl at C(3) is in an equatorial position. The phenyl group at C(6) is equatorially situated in both molecules



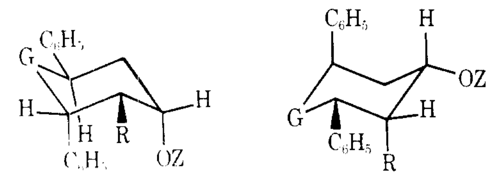
in the solid state.

Stereochemistry of Reduction with $LiAlH_4$. The reduction of ketones **3b–e** was carried out using $LiAlH_4$ in ether. A summary of these results to give **7–9** are in Tables I and V. It will be seen that on reduction with $LiAlH_4$ the thianone **3b** afforded predominantly the more stable equatorial alcohol **7a** along with axial alcohol **8a** presumably with the structures



7 **8**

a, G = S; R′ = R″ = R⁗ = H; R = R‴ = p-$CH_3OC_6H_4$; Z = H
b, G = S; R′ = R″ = H; R = R‴ = C_6H_5; R⁗ = CH_3; Z = H
c, G = S; R′ = R″ = H; R = R‴ = C_6H_5; R⁗ = C_2H_5; Z = H
d, G = S; R = C_6H_5; R′ = R⁗ = H; R″ = R‴ = CH_3; Z = H
e, G = SO_2; R′ = R″ = R⁗ = H; R = R‴ = p-$CH_3OC_6H_4$; Z = H
f, G = SO_2; R′ = R″ = H; R = R‴ = C_6H_5; R⁗ = CH_3; Z = H
g, G = SO_2; R′ = R″ = H; R = R‴ = C_6H_5; R⁗ = C_2H_5; Z = H
h, G = S; R′ = R″ = H; R = R‴ = C_6H_5; R⁗ = CH_3; Z = C(O)CH_3
i, G = S; R′ = R″ = H; R = R‴ = C_6H_5; R⁗ = C_2H_5; Z = C(O)CH_3
j, G = SO_2; R′ = R″ = H; R = R‴ = C_6H_5; R⁗ = CH_3; Z = C(O)CH_3
k, G = SO_2; R′ = R″ = H; R = R‴ = C_6H_5; R⁗ = C_2H_5; Z = C(O)CH_3

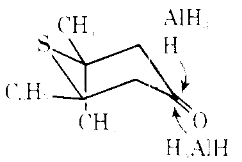


9 9'

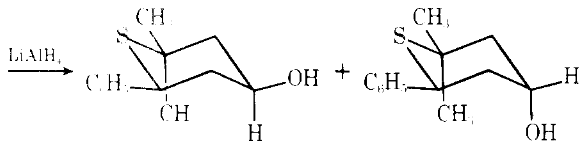
a, G = S; R = CH_3; Z = H
b, G = S; R = C_2H_5; Z = H
c, G = SO_2; R = CH_3; Z = H
d, G = SO_2; R = C_2H_5; Z = H
e, G = S; R = CH_3; Z = C(O)CH_3
f, G = S; R = C_2H_5; Z = C(O)CH_3
g, G = SO_2; R = CH_3; Z = C(O)CH_3
h, G = SO_2; R = C_2H_5; Z = C(O)CH_3

shown. However, $LiAlH_4$ reduction of thianones **3c–e** afforded a more severe mixture of the axial and equatorial alcohols.

The reduction of **3e** with $LiAlH_4$ produced epimeric alcohols **7d** (45%) and **8d** (47%). The small preponderance of the less stable axial alcohol **8d** in the reduction of **3e** may indicate



3e



7d 8d

that the axial methyl group in **3e** slightly hinders the approach of the reagent from the axial side. Preferential approach of the hydride from the equatorial side should therefore lead to more of the less stable thianol **8d** with an axial hydroxyl group. The ratio is similar to that for the axial (55%) and equatorial (45%) isomers reported for the $LiAlH_4$ reduction of analogously constituted 3,3,5-trimethylcyclohexanone.[17]

The reduction of each of the thianones **4b** and **4c** with $LiAlH_4$ gave exclusively one alcohol (**9a** or **9b**). IR and NMR analysis of these alcohols and kinetics of acetylation[18] indicated an equatorial orientation of the hydroxyl group in both cases. Scale models suggest hindrance to the axial approach to the hydride ion, and the exclusive formation of the equatorial alcohols was surprising. However, a similar observation was made by Baliah and co-workers,[19] who observed mostly equatorial alcohol (90%) in the reduction via $LiAlH_4$ of *trans*-2,6-diphenyl-4-thianone (**4a**). Although alcohols **9a** and **9b** seem reasonable as illustrated, a preliminary X-ray diffraction analysis of single crystals of the ethyl compound indicates that the structure is **9b**.[18] Thus, in the reduction of **4c**, hydride transfer may come via an equatorial approach and the resulting alcohol may then undergo ring reversal to give **9b**. The same appears true for **4b** → **9a'**, now under study.

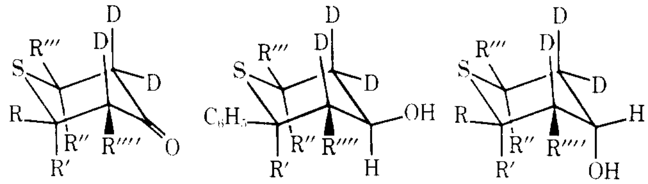
Oxidation of thianones **3c**, **3d**, **4b**, and **4c** with H_2O_2 yields the sulfones **5a**, **5b**, **6a**, and **6b**, respectively. Also with H_2O_2 thianols **7a**, **7b**, **7c**, **8a**, **8b**, and **8c** give sulfones **7e–g** and **8e–g**. The acetates **7j** and **7k** as well as **8j** and **8k** are easily prepared for characterization purposes from **7f**, **7g**, **8f**, and **8g**. Similar derivatives of the trans alcohol **9** (recall that the structures may be better represented as **9'**) are found in Table IV also.

In order to simplify the spectral analysis for reduction products therefrom, **3a** was deuterated at the α positions to give **10a**. The same procedure gave ketones **10b** and **10c** from **3c** and **3e**, respectively. Reduction of **10a** with $LiAlH_4$ in ether produced **11b** and **12b** in a 1.84:1 ratio similar to that found

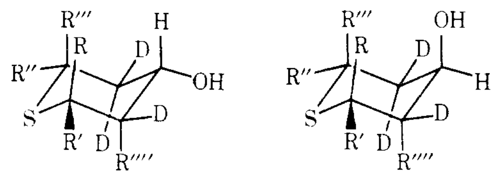
Table I. Substituted 4-Thianols and Corresponding Acetates

compd	IR C–O stretch, cm^{-1}	yield, %	mp, °C	formula[f]
7a		*e*	194–195[a]	$C_{19}H_{22}O_3S$
7b		*e*	154–155[a]	$C_{18}H_{20}OS$
7c		*e*	124–126[b]	$C_{19}H_{22}OS$
7d		*e*	93–94[a]	$C_{13}H_{18}OS$
7h	1031	70	97–98[a]	$C_{20}H_{22}O_2S$
7i	1036	70	114–116[a]	$C_{21}H_{24}O_2S$
8a		*e*	160–161[a]	$C_{19}H_{22}O_3S$
8b		*e*	157–158[a]	$C_{18}H_{20}OS$
8c		*e*	89–90[c]	$C_{19}H_{22}OS$
8d		*e*	64–65[a]	$C_{13}H_{18}OS$
8h	1020	68	88–89[a]	$C_{20}H_{22}O_2S$
8i	1020	73	119–121[d]	$C_{21}H_{24}O_2S$
9a		*e*	144–146[a]	$C_{18}H_{20}OS$
9b		*e*	121–122[a]	$C_{19}H_{22}OS$
9e	1038	76	133–135[d]	$C_{20}H_{22}O_2S$
9f	1038	84	106–107[a]	$C_{21}H_{24}O_2S$

[a] Recrystallized from aqueous ethanol. [b] Recrystallized from benzene–petroleum ether (60–80 °C). [c] Recrystallized from hexane. [d] Recrystallized from ethanol. [e] The yields for the thianols depend upon the reducing conditions (see Table V). [f] Satisfactory analytical values (±0.35% for C, H, or C, H, S) were reported for all compounds (Ed.).



10 11 12



11' 12'

a, R = R''' = C_6H_5; R' = R'' = H; R'''' = D
b, R = R''' = C_6H_5; R' = R'' = H; R'''' = CH_3
c, R = C_6H_5; R' = H; R'' = R''' = CH_3; R'''' = D

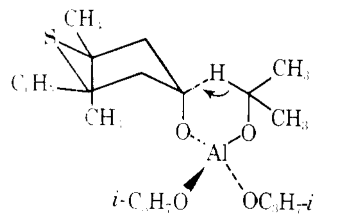
in a similar reduction of **3b** → **7b** + **8b** (Table V). In view of the finding[18] that **4e** gave **9b**, we cannot eliminate from consideration that **11'** and **12'** may be the products from reduction of **10b** rather than **11b** and **12b**, and this will be investigated.

Meerwein–Ponndorf–Verley Reduction of 4-Thianones. Under Meerwein–Ponndorf–Verley (MPV) reduction conditions using aluminum isopropoxide and isopropyl alcohol, each of the 4-thianones **3b–c** afforded isomeric alcohols (Table V). On chromatography over alumina, the axial alcohols were eluted first. In general, cyclohexanols with an equatorial hydroxyl group are more strongly adsorbed than those with an axial hydroxyl group.[20–22] Generally, the MPV reduction is considered to proceed through a cyclic transition state.[23,24] On this basis,[23,24] two cyclic transition states (**13** and **14**) can be envisioned for the reduction of thianone **3e**. Courtauld models revealed a greater steric hindrance to the axial approach of the hydride in **14** than to the equatorial approach in **13**. Accordingly, it is reasonable that thianone **3e**, with the ring anchored in a single chair conformation, should lead to more of the axial alcohol **8d** than that with an equatorial alcohol **7d**. These expectations are confirmed in the

Table II. IR and ^{1}H NMR Data[a] for Substituted 4-Thianols

compd	IR C–O stretch, cm^{-1}	H(2)	H(3)	H(4)	H(5)	H(6)	other
7a	1040	4.06 (dd)	1.65–2.57 (m)	3.82 (s)			1.56 (s, 1 H, OH) 3.73 (s, 6 H, OCH_3) 6.70–6.78 (d, 4 H, Ar H) 7.25–7.35 (d, 4 H, Ar H)
7b	1025	3.71 (d) J = 11.50 Hz	2.41–2.60 (m)	3.44 (t)[b] ($W_{1/2}$ = 20.0 Hz)	2.00–2.35 (m)	4.12 (dd) J = 2.5 Hz J = 10.0 Hz	0.88 (d, 3 H, CH_3) 1.92 (s, 1 H, OH) 7.20–7.42 (m, 10 H, Ar H)
7c	1041	3.98 (d) J = 11.0 Hz	2.48–2.66 (m)	3.70 (t)[b] ($W_{1/2}$ = 20.0 Hz)	1.94–2.40 (m)	4.10 (dd) J = 2.5 Hz J = 10.0 Hz	0.77 (t, 3 H, CH_2**CH_3**) 1.10–1.50 (m, 2 H, **CH_2**CH_3) 1.67 (s, 1 H, OH) 7.20–7.40 (m, 10 H, Ar H)
7d	1040		1.78 (t) J = 6.0 Hz	3.78–4.08 (m)	1.98–2.15 (m) 2.44–2.52 (m)	4.03 (dd)	1.34 [s, 3 H, CH_3(a)] 1.47 [s, 3 H, CH_3(e)] 1.60 (s, 1 H, OH) 7.19–7.42 (m, 5 H, Ar H)
8a	1031	4.44–4.59 (m)	2.11–2.25 (m)	4.44 (s) overlapped with H(2,6)			1.61 (s, 1 H, OH) 3.77 (s, 6 H, OCH_3) 6.78–6.87 (d, 4 H, Ar H) 7.24–7.32 (d, 4 H, Ar H)
8b	990	4.21 (d) J = 12.0 Hz	2.36 (m)	4.13 (br s) ($W_{1/2}$ = 7.0 Hz)	2.15–2.30 (m)	4.58 (dd) J = 5.0 Hz J = 10.0 Hz	0.82 (d, 3 H, CH_3) J = 7.00 Hz 1.78 (s, 1 H, OH) 7.20–7.42 (m, 10 H, Ar H)
8c	1020	4.27 (d) J = 11.0 Hz	2.40–2.56 (m)	4.44 (br s) ($W_{1/2}$ = 7.0 Hz)	1.88–2.18 (m)	4.60 (dd) J = 5.0 Hz J = 12.0 Hz	0.77 (t, 3 H, CH_2**CH_3**) 1.10–1.50 (m, 2 H, **CH_2**CH_3) 7.20–7.44 (m, 10 H, Ar H)
8d	1040 1018		1.88 (t) J = 4.5 Hz	overlapped with H(6)	2.08–2.12 (m)	4.33–4.48 (m)	1.24 [s, 3 H, CH_3(e)] 1.66 [s, 3 H, CH_3(a)] OH overlapped with CH_3(a) 7.19–7.48 (m, 5 H, Ar H)
9a	1066	4.12 (d) J = 3.0 Hz	2.18–2.28 (m)	3.91 (quint)	2.30–2.46 (m)	4.34 (t) J = 5.0 Hz	0.96 (d, J = 7 Hz, 3 H, CH_3) 1.60 (s, 1 H, OH) 7.20–7.70 (m, 10 H, Ar H)
9b	1054	4.10 (d) J = 5.0 Hz	2.04–2.25 (m)	overlapped with H(2)	2.39 (t) J = 5.0 Hz	4.51 (t) J = 5.0 Hz	0.77 (t, 3 H, CH_2**CH_3**) 1.22–1.7 (m, 2 H, **CH_2**CH_3) 7.18–7.64 (m, 10 H, Ar H)

[a] NMR values are in δ. Abbreviations used: s, singlet; d, doublet; dd, doublet of doublet; t, triplet; m, multiplet; quint, quintet. [b] Complex triplet.



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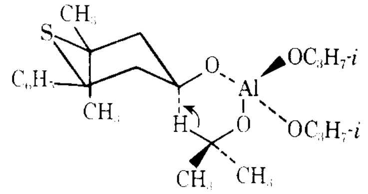

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present study (see Table V). As the apparent degree of steric hindrance around the carbonyl increases, owing to the proximity of the bulky alkyl groups, the yield of the axial isomer *increases*. This is supported by the present investigation. In contrast to the above observation, Hardy and Wicker[25] report a high yield (75%) of *cis*-3,3,5-trimethylcyclohexanol (with an equatorial hydroxyl) in the reduction of 3,3,5-trimethylcyclohexanone by the MPV method. However, in analyzing the isomer ratio of the products, the possibility of isomerization of the less stable axial alcohol to a more stable epimer under equilibrating conditions (aluminum isopropoxide–isopropyl alcohol) should be examined. In order to substantiate this, the axial thianols have been allowed to equilibrate under MPV conditions employing aluminum isopropoxide, isopropyl alcohol, and acetone for 140 h. It is found that thianols **8a–d** epimerize to the corresponding equatorial isomers, which are obtained in high yield after chromatography of the equilibration mixture. However, it is also observed that *no epimerization* occurs during MPV reduction in the present study (within a reaction time of 6 h). It is noteworthy also that thianones **4b** and **4c** gave exclusively the alcohol with the equatorially substituted hydroxyl group as discussed from the same reduction with $LiAlH_4$.

Stereochemistry of the 4-Thianols. It has been demonstrated that the carbon–oxygen stretching frequency for an equatorial hydroxy group (near 1040 cm^{-1}) is greater than that for an axial hydroxy group (1000 cm^{-1}).[26-28] The C–O stretching frequencies for the thianols are listed in Table II. The observation of the position of this band can be of considerable aid in the determination of the stereochemical configuration of the hydroxyl group in the 4-thianols. It can be seen from Table II that the thianols with an equatorial hydroxyl group give an absorption band at higher frequency compared to its epimer with an axial hydroxyl group.

The stereochemistry of the thianols has been further confirmed by a study of their ^{1}H NMR spectra and kinetics of

Table III. Physical Data for 4-Thianone 1,1-Dioxides

compd	IR, cm^{-1} C=O	$-SO_2-$ asym	$-SO_2-$ sym	yield, %	mp, °C	formula[b]
5a	1721	1326	1136	80[a]	201–203	$C_{18}H_{18}O_3S$
5a	1721	1330	1138	90[a]	202–204	$C_{19}H_{20}O_3S$
6a	1709	1318	1124	85[a]	202–204	$C_{18}H_{18}O_3S$
6b	1718	1318	1126	86[a]	171–173	$C_{19}H_{20}O_3S$

[a] Crystallized from aqueous ethanol. [b] Satisfactory analytical values (±0.3% for C, H) were reported for all compounds (Ed.).

Table IV. 4-Thianol 1,1-Dioxides and Corresponding Acetates

compd	IR, cm^{-1} C–O	$-SO_2-$ asym	$-SO_2-$ sym	yield, %	mp, °C	formula[c]
7e	1064	1297	1130	80	295–297[a]	$C_{19}H_{22}O_5S$
7f	1010	1370	1149	72	282–283[a] (dec)	$C_{18}H_{10}O_3S$
7g	1058	1307	1136	88	234–236[b]	$C_{19}H_{22}O_3S$
7j	1041	1295	1135	72	252–253[a]	$C_{20}H_{22}O_4S$
7k	1038	1312	1134	83	189–191[b]	$C_{21}H_{24}O_4S$
8e	1031	1300	1134	78	222–224[a]	$C_{19}H_{22}O_5S$
8f	1003	1299	1149	80	338–341[a]	$C_{18}H_{20}O_3S$
8g	1026	1294	1133	86	264–266[b]	$C_{19}H_{22}O_3S$
8j	1020	1316	1138	70	185–187[a]	$C_{20}H_{22}O_4S$
8k	1027	1299	1142	81	194–196[a]	$C_{21}H_{24}O_4S$
9c	1065	1295	1117	77	198.5–201.5[b]	$C_{18}H_{20}O_3S$
9d	1064	1295	1117	90	217–219.5[b]	$C_{19}H_{22}O_3S$
9g	1045	1300	1125	67	206–208[a]	$C_{20}H_{22}O_4S$
9h	1050	1302	1124	86	200–201[a]	$C_{21}H_{24}O_4S$

[a] Recrystallized from ethanol. [b] Recrystallized from aqueous ethanol. [c] Satisfactory analytical values (±0.3% for C, H) were reported for all compounds.

Table V. Composition of the Products from the Reduction of 4-Thianones

thianones reduced	total crude product, %	unreduced thianone, %	yield (%) of epimeric thianols axial	equatorial
		reduction with MPV		
3b	90		50 (**8a**)	15 (**7a**)
3c	87	8	66 (**8b**)	13 (**7b**)
3d	98	4	65 (**8c**)	20 (**7c**)
3e	92	3	76 (**8d**)	10 (**7d**)
4b	98	25		71 (**9a**)
4c	95	50		43 (**9b**)
		reduction with $LiAlH_4$		
3b	95		3	90
3c	92	8	15	35
3d	94	4	31	56
3e	96	2	47	45
4b	94	2		91
4c	96	3		92

acetylation with acetic anhydride in pyridine.[18] The ^{1}H NMR spectral data of the epimeric thianols are summarized in Table II. Significant information regarding the configuration of the hydroxyl group may be deduced from the chemical shift data of the H(4) proton. The points of interest in these spectra are the half-widths of bands for the H(4) hydrogen.[29] It can be seen from Table II that the half-width signals for axial alcohols **8b** and **8c** are 7 Hz as compared to about 20 Hz for the corresponding equatorial epimers **7b** and **7c**. The H(4) axial hydrogens of the equatorial alcohols **7b** and **7c** are more strongly coupled with the neighboring hydrogens than are the equatorial H(4) hydrogens in axial alcohols **8b** and **8c**. The spectra of the equatorial thianols **7b** and **7c** also show signals for the H(4) axial hydrogen more downfield compared to those for the epimeric axial alcohols with an equatorial H(4) hydrogen (see Table II).

Single-Crystal Analysis of 4b and 4c. Single crystals of **4b** and **4c**, mp 150–152 and 120–121 °C, respectively, were grown from different solvents. The basic stereochemistry of both sulfides is identical as shown in the stereoview of single molecules in Figure 1. Axial disposition of the phenyl group occurs at C(2) in each system along with an equatorial phenyl group at C(6). An equatorial methyl or ethyl substituent is confirmed at C(3) in **4b** and **4c**, respectively. Figure 2 contains the bond distances, while Figure 3 displays the corresponding bond angles. Torsional angles are given in Table VI. Average torsional angles of 55.5 and 55.0° for **4b** and **4c**, respectively, are slightly smaller than that reported for cyclohexane (55.9°)[30a] but larger than that observed in 4-*tert*-butylcyclohexanone (52°).[30b] A comparison of bond lengths of identical bonds in **4b** and **4c** showed differences of less than 3 estimated standard deviations with the exception of C(8)–C(9) and C(7)–C(12) bonds. Greater deviations occur in the comparison of bond angles, but the values are not abnormal.

A common plane includes C(2), C(3), C(5), and C(6) in both systems with the S 0.93 Å above the plane and C(4) at 0.56 Å below the plane in **4b**. Values of 2.52 ± 0.04 and 2.66 Å were determined for the H(12)–C(4) distances in **4b** and **4c**, respectively, indicating that the axial phenyl ring is directed with a side toward C(4). Consequently, the deshielding of C(4) is not unreasonable in the ^{13}C NMR spectra of the two thianones (209.87 and 209.55 ppm, respectively) as compared to the chemical shifts for C(4) in the all-equatorially substituted isomers **3c** (208.59 ppm) and **3d** (208.73 ppm).[1]

The ^{1}H NMR analysis of **3c** reveals a $J_{H(2a),H(3a)} = 11$ Hz while **4b** had a $J_{H(2e),H(3a)} = 5$ Hz, which is in fairly good agreement for an axial–axial and equatorial–axial arrange-

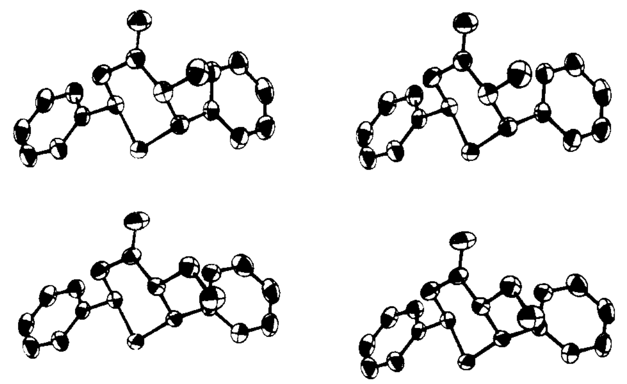

Figure 1. Stereoview of single molecules of (a) **4b** and (b) **4c**.

Table VI. Final Torsion Angles (deg)

	4b	4c
S(1)-C(2)-C(3)-C(4)	−57	−55
C(2)-C(3)-C(4)-C(5)	51	52
C(3)-C(4)-C(5)-C(6)	−52	−54
C(4)-C(5)-C(6)-S(1)	58	58
C(5)-C(6)-S(1)-C(2)	−58	−56
C(6)-S(1)-C(2)-C(3)	57	55
C(6)-S(1)-C(2)-C(7)	−75	−78
C(4)-C(3)-C(2)-C(7)	72	76
S(1)-C(2)-C(7)-C(8)	−84	−90
S(1)-C(2)-C(7)-C(12)	93	88
C(3)-C(2)-C(7)-C(8)	147	139
C(3)-C(2)-C(7)-C(12)	−35	−43
C(2)-S(1)-C(6)-C(15)	179	181
C(4)-C(5)-C(6)-C(15)	−179	−179
S(1)-C(6)-C(15)-C(16)	−150	−152
S(1)-C(6)-C(15)-C(20)	33	31
C(5)-C(6)-C(15)-C(16)	87	85
C(5)-C(6)-C(15)-C(20)	−90	−92
S(1)-C(2)-C(3)-C(13)	173	177
C(5)-C(4)-C(3)-C(13)	−180	−179
C(2)-C(3)-C(4)-O(14)	−133	−132
C(6)-C(5)-C(4)-O(14)	132	130
C(7)-C(2)-C(3)-H(3)	−177	−173

ment of hydrogen on C(2) and C(3) in the respective systems.[14,31] In the ethyl analogues **3d** and **4c**, the related values are $J_{H(2a),H(3a)}$ = 11 Hz and $J_{H(2e),H(3a)}$ = 6 Hz, respectively. Torsional angles of H(2)-C(2)-C(3)-H(3) in **4b** and **4c** are 56 and 59°. In **4b** and **4c**, the internal angle S(1)-C(2)-C(3)-C(4) is 57 and 55° (Table VI), respectively; these values lie on both sides of that (56°) for cyclohexane.[32] This does suggest that the ethyl group at C(3) in **4c** experiences a greater steric interaction with the axial phenyl group at C(2) than is true between the methyl and the corresponding phenyl group in **4b**. That the rings are flattened is shown by the internal angles C(2)-C(3)-C(4)-C(5), which are 51 and 52°, respectively, which is to be expected for the end of the molecule which contains the carbonyl function. That there is interaction involving the alkyl and axial phenyl groups is also supported by the identical angles (58°) for C(4)-C(5)-C(6)-S(1) in both of these systems of **4b** and **4c**. Moreover, since the rings are slightly flattened and the S-C(2) bond is considerably longer than S-C(6) in **4b**, we tentatively conclude that a similar situation may persist in **3c** and that the torsion angle H(2a)-C(2)-C(3)-H(3a) is probably not distorted much from 180°; this is supported by the experimental $J_{H(2a),H(3a)}$, value of 11.5 Hz ($DCCl_3$) for **3c**.

Interestingly, the H(12)-C(13) distances in **4b** and **4c** were calculated to be 3.33 and 3.14 Å (SD = 0.05 Å), respectively.

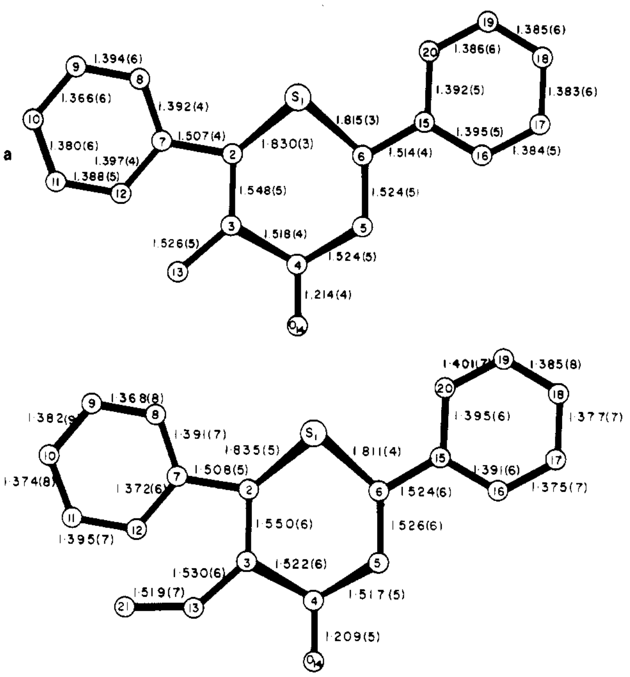

Figure 2. Bond distances (Å) for (a) **4b** and (b) **4c**. Calculated standard deviations are given in parentheses.

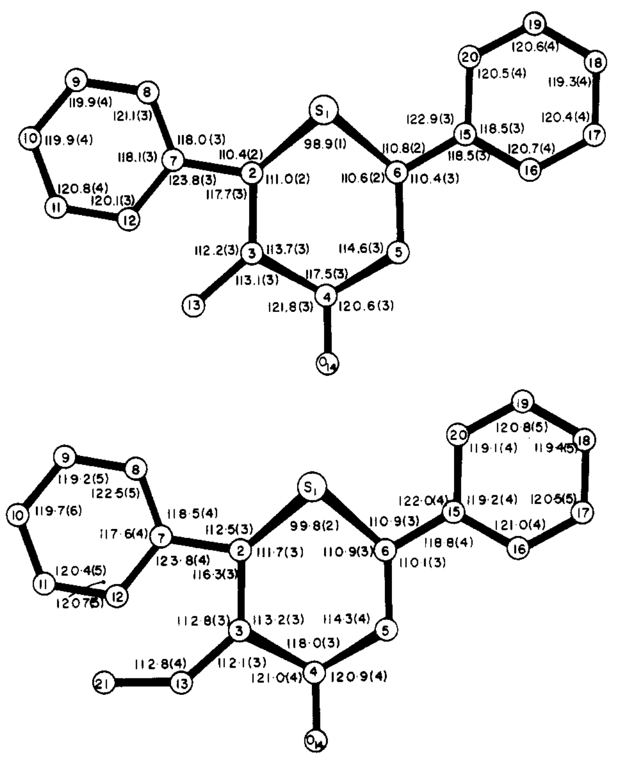

Figure 3. Bond angles (deg) for (a) **4b** and (b) **4c**.

Courtauld models imply that the edge of the axial phenyl ring at C(2) may lie nearly between C(3) and C(4), which is supported by the above distances and those given previously for H(12)-C(4) in **4b** and **4c**. In contrast, the H(6)-H(12) distances were calculated as 2.39 and 2.48 Å in the isomers, attesting to the closeness of H(6) and the phenyl ring at C(2). Calculated distances between H(6) and the face of the phenyl ring at C(2) are 2.22 and 2.07 Å, respectively. Again the standard deviation is high ($\simeq$0.05 Å), but nevertheless these distances are sufficiently short to be inside van der Waals contact radii. Unfortunately, the ^{1}H NMR signals for the two protons at H(5) and H(6) are complex in both **4b** and **4c** and prevent correlation of the size of ^3J with the dihedral angle H(5a)–C(5)–C(6)–H(6a).

A very novel feature of structures **4b** and **4c** is the unequal C–S bond lengths within each compound. These differences, Δ = 0.015 and 0.024 Å, are about 5–6 standard deviations and must be considered significant. Differences in C–S bond lengths are reported for a variety of sulfur compounds, but the significance of these differences varies greatly even within groups of similar compounds. In studies of a series of four sulfur-containing ribopyranosides,[33] differences as small as 0.008 Å (1.6σ) and as large as 0.041 Å (6.8σ) were observed. Similarly, differences as small as 0.001 Å (0.2σ) and as large as 0.046 Å (15.3σ) have been recently reported for a series of sulfoxide structures.[34a] A satisfactory explanation dealing comprehensively with this effect and its variability is not available. It is possible that in **4b** and **4c** there is some repulsive interaction between the axial phenyl group and the nonbonding electron pair on sulfur which results in an elongated S(1)–C(2) bond. We note that the angle of the benzene ring attached at C(6) to the plane composed of C(2), C(3), C(5), and C(6) atoms is 81.5° in **4b** and 79.7° in **4c** with C(20) in both compounds tilted toward S(1). Courtauld models of this arrangement imply that the p orbital on C(20) may interact with the sulfur atom, possibly via delocalization into d orbitals. This might cause a compression effect, resulting in a shortened S(1)–C(6) bond. Comparing the observed C–S distances with that of 1.817 (5) Å given by Sutton[34b] as the mean for a paraffinic C–S distance and those observed for trithiane (1.816 Å)[34c] indicates that the C(2)–S distances in **4b** and **4c** are more elongated than the C(6)–S distances are shortened.

Experimental Section

General Data. Melting points were determined with a Thomas-Hoover capillary apparatus and are uncorrected. NMR spectra were recorded in parts per million downfield from Me_4Si on a Varian HR resolution XL-100(15) NMR spectrometer with a TT-100 FT accessory. Infrared and mass spectral data were collected on a Beckman IR-5A unit and a CEC Model 21 HR unit, respectively. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

The ketones **3a**,[19] **3b**,[19] and **4a**[35] were prepared by known methods. All solvents used were reagent grade.

2-Ethyl-1,5-diphenyl-1,4-pentadien-3-one (2d). A solution of sodium hydroxide (12.5 g, 0.31 mol) in water (50 mL) was added slowly to an ice-cold solution of 20 g (0.114 mol) of 3-ethyl-4-phenyl-3-buten-2-one (**1b**)[36] and 15 g (0.141 mol) of benzaldehyde in 75 mL of ethanol. The resulting mixture was stirred at room temperature for 4 h and poured into water (500 mL). The basic solution was acidified (glacial AcOH) and extracted (ether). The extracts were combined, washed with a saturated solution of bicarbonate and water, and dried (Na_2SO_4). Removal of the solvent and vacuum distillation of the residue gave 19.8 g (65.7%) of **2d**: bp 180–182 °C (0.45 mm); IR (neat) 1645 and 1605 cm^{-1}; ^{1}H NMR ($DCCl_3$) δ 1.13 (t, 3 H, CH_2**CH_3**), 2.40–2.80 (m, 2 H, **CH_2**CH_3), 7.2–7.4 (m, 13 H, Ar H and vinylic H).

Anal. Calcd for $C_{19}H_{18}O$: C, 86.98; H, 6.91. Found: C, 86.88; H, 7.21.

2-Methyl-1,5-diphenyl-1,4-pentadien-3-one (2c). The compound, bp 180–182 °C (0.45 mm), was obtained from **1a**[37] (64.5%) following the procedure used for compound **2d** described above: IR (neat) 1645 and 1605 cm^{-1}; ^{1}H NMR ($DCCl_3$) δ 1.19 (s, 3 H, CH_3), 7.20–7.62 (m, 13 H, Ar H and vinylic H).

Anal. Calcd for $C_{18}H_{16}O$: C, 87.06; H, 6.49. Found: C, 87.28; H, 6.62.

***r*-2,*cis*-6-Diphenyl-*trans*-3-methyl-4-thianone (3c).** Gaseous H_2S was passed into a boiling mixture of **2c** (40 g, 0.16 mol) and $CH_3CO_2Na{\cdot}3H_2O$ (40 g, 0.29 mol) in 400 mL of ethanol for 15 h. The reaction mixture was cooled to room temperature and kept at 0 °C for 2 h. The resinous matter was filtered, and the alcoholic solution was kept in a refrigerator for 3 days. The white solid that formed was filtered and recrystallized from petroleum ether (60–80 °C), yielding 11 g (25%) of **3c**: mp 123–125 °C; IR (KBr) 1701 cm^{-1} (C=O); ^{1}H NMR ($DCCl_3$) δ 1.14 (d, J = 7 Hz, 3 H, CH_3), 3.9 [d, J = 11.5 Hz, 1 H, H(2)], 3.18 [m, 1 H, H(3)], 2.90–3.06 [m, 2 H, H(5)], 4.24 [dd, J = 3.5 and 11.5 Hz, 1 H, H(6)], 7.20–7.42 (m, 10 H, Ar H); mass spectrum, m/e (rel intensity) 282 (M$^+$, 53).

Anal. Calcd for $C_{18}H_{18}OS$: C, 76.55; H, 6.42; S, 11.35. Found: C, 76.32; H, 6.40; S, 11.50.

Oximation under standard conditions gave a product, mp 203–205 °C, after recrystallization from aqueous ethanol.

Anal. Calcd for $C_{18}H_{19}NOS$: C, 72.69; H, 6.44. Found: C, 72.80; H, 6.49.

The semicarbazone crystallized from aqueous ethanol, mp 215–216 °C.

Anal. Calcd for $C_{19}H_{21}N_3OS$: C, 67.22; H, 6.23. Found: C, 67.58; H, 6.02.

***r*-2,*trans*-6-Diphenyl-*cis*-3-methyl-4-thianone (4b).** Into a boiling solution of sodium acetate trihydrate (40 g, 0.29 mol) and **2c** (25 g, 0.01 mol) in methanol (200 mL) was passed a steady and fast stream of H_2S for 4 h. The passage of H_2S was continued at room temperature until white, shining crystals appeared. The alcoholic layer was decanted off from the resinous matter and kept at 0 °C for 1 h. White crystals formed and were filtered and recrystallized (ethanol) to yield 7.5 g (26%) of **4b**: mp 151–152 °C; IR (KBr) 1692 cm^{-1} (C=O); ^{1}H NMR ($DCCl_3$) δ 1.15 (d, J = 7 Hz, 3 H, CH_3), 3.07–3.37 [m, 3 H, H(3), H(5)], 4.27–4.43 [m, 2 H, H(2), H(6)], 7.08–7.34 (m, 10 H, Ar H); ^{1}H NMR (pyridine) δ 1.15 (d, J = 7 Hz, 3 H, CH_3), 3.14–3.50 [m, 3 H, H(3), H(5)], 4.57 [d, J = 5 Hz, 1 H, H(2)], 4.48–4.73 [m, 1 H, H(6)]; mass spectrum, m/e (rel intensity) 282 (M$^+$, 37).

Anal. Calcd for $C_{18}H_{18}OS$: C, 76.55; H, 6.42; S, 11.35. Found: C, 76.72; H, 6.57; S, 11.60.

Oximation gave a solid which was recrystallized from aqueous ethanol, mp 156–158 °C.

Anal. Calcd for $C_{18}H_{19}NOS$: C, 72.69; H, 6.44. Found: C, 72.76; H, 6.60.

***r*-2,*cis*-6-Diphenyl-*trans*-3-ethyl-4-thianone (3d).** To a solution of 2-ethyl-1,5-diphenyl-1,4-pentadien-3-one (**2d**; 40 g, 0.15 mol) in ethanol (400 mL) was slowly added Triton B (5 mL) with cooling. The mixture was then heated under reflux and H_2S was passed into it for 15 h. The reaction mixture was cooled (0 °C) for 24 h and the resinous matter was filtered. The alcoholic solution was kept in a refrigerator for 3 days, whereupon colorless crystals of **3d** separated. The solid was filtered off, dried, and recrystallized [petroleum ether (60–80 °C)] to give 17 g (38%) of **3d**: mp 74–75 °C; IR (KBr)[1] 1701 cm^{-1} (C=O); ^{1}H NMR ($DCCl_3$) δ 0.79 (t, 3 H, $-CH_2CH_3$), 1.10–1.8 (m, 2 H, $-$**CH_2**CH_3), 4.02 [d, J = 11.0 Hz, 1 H, H(2)], 3.15 [d, J = 11 Hz, 1 H, H(3)], 2.82–3.11 [m, 2 H, H(5)], 4.33 [dd, 1 H, H(6)], 7.22–7.42 (m, 10 H, Ar H); mass spectrum, m/e (rel intensity) 296 (M$^+$, 69).

Anal. Calcd for $C_{19}H_{20}OS$: C, 76.98; H, 6.80; S, 10.81. Found: C, 77.02; H, 6.96; S, 10.49.

The oxime melted at 148–149 °C after recrystallization from aqueous ethanol.

Anal. Calcd for $C_{19}H_{21}NOS$: C, 73.27; H, 6.79. Found: C, 73.45; H, 6.82.

The semicarbazone was crystallized from aqueous ethanol, mp 205–206 °C.

Anal. Calcd for $C_{20}H_{23}N_3OS$: C, 67.95; H, 6.55. Found: C, 67.63; H, 6.70.

***r*-2,*trans*-6-Diphenyl-*cis*-3-ethyl-4-thianone (4c).** Into a boiling solution of **2d** (25 g, 0.095 mol), sodium acetate (40 g, 0.29 mol), and methanol (200 mL) was passed H_2S for 4 h. Thereafter, the passage of H_2S was continued at room temperature until white crystals appeared. The supernatant solution was removed from the resinous material and kept at 0 °C for 1 h. A solid formed and was filtered off, dried, and recrystallized (ethanol) to give 8 g (28%) of **4c**: mp 120–121 °C; IR (KBr) 1695 cm^{-1} (C=O); ^{1}H NMR ($DCCl_3$) δ 0.82 (t, 3 H, CH_2CH_3), 1.28 (septet, 0.5 CH_2CH_3), 2.03 (septet, 0.5 CH_2CH_3), 2.92–3.10 [m, 3 H, H(3), H(5)], 4.47 [d, J = 5 Hz, 1 H, H(2)], 4.27–4.42 [(m, 1 H, H(6)], 7.12–7.42 (m, 10 H, Ar H); ^{1}H NMR (pyridine) δ 1.27 (septet, 0.5 **CH_2**CH_3), 2.05 (septet, 0.5 **CH_2**CH_3), 3.04–3.45 [m, 3 H, H(3), H(5); d, 1 H, J = 6 Hz, H(2)], 4.50–4.67 [m, 1 H, H(6)]; mass spectrum, m/e (rel intensity) 296 (M$^+$, 35).

Anal. Calcd for $C_{19}H_{20}OS$: C, 76.98; H, 6.80; S, 10.81. Found: C, 76.81; H, 6.72; S, 11.04.

Oximation under the usual conditions gave a product, mp 141–143 °C, after recrystallization (aqueous ethanol).

Anal. Calcd for $C_{19}H_{21}NOS$: C, 73.27; H, 6.79. Found: C, 72.81; H, 7.10.

2,2-Dimethyl-6-phenyl-4-thianone (3e). Into a boiling solution of sodium acetate trihydrate (40 g, 0.29 mol), 1-phenyl-5-methyl-1,4-hexadien-3-one (**2e**; 50 g, 0.268 mol), and ethanol (300 mL) was passed H_2S for 8 h. The reaction mixture was then poured into water

(1000 mL), extracted with ether (3 × 200 mL), and dried (Na_2SO_4). The solution was filtered and concentrated, and the residue was distilled to yield 48.2 g (81.5%) of **3e**, bp 140–143 °C (0.9 mm). The light yellow viscous oil solidified upon standing and was recrystallized from petroleum ether (60–80 °C): mp 45–46 °C (lit.[38] mp 42 °C); IR (KBr) 1698 cm^{-1} (C=O); ^{1}H NMR ($DCCl_3$) δ 1.51 [s, 3 H, CH_3(a)], 1.54 [s, 3 H, CH_3(e)], 2.56 [t, 2 H, H(3)], 2.80 [s, 1 H, H(5e)], 2.88 [d, J = 4 Hz, 1 H, H(5a)], 7.24–7.40 (m, 5 H, Ar H); mass spectrum, m/e (rel intensity) 220 (M^+, 50).

The oxime was recrystallized from aqueous methanol, mp 158–159 °C.

Anal. Calcd for $C_{13}H_{17}NOS$: C, 66.34; H, 7.28. Found: C, 66.21; H, 7.50.

The semicarbazone melted at 190–192 °C after recrystallization (ethanol).

Anal. Calcd for $C_{14}H_{19}N_3OS$: C, 60.61; H, 6.90. Found: C, 60.49; H, 7.02.

1-Phenyl-5-methyl-1,4-hexadien-3-one (2e). A modified procedure[39] for **2e** was used in this experiment. To a mixture of mesityl oxide (43 g, 0.44 mol), benzaldehyde (78 g, 0.74 mol), hydroquinone (0.5 g), and piperidine (5 mL) was added acetic acid (5 mL), and the mixture was heated (100 °C) under N_2 for 24 h. The solution was then poured onto crushed ice and extracted with ether (3 × 200 mL). The ethereal layer was washed with water and sodium bicarbonate (5%) solution and dried (Na_2SO_4). Evaporation of ether left a dark red oil. Fractional distillation yielded 60 g (85%) of **2e**: bp 130–133 °C (0.7 mm) [lit.[39] bp 172–175 °C (11 mm)]; IR (film) 1667 (C=O) and 1630 (C=C) cm^{-1}; ^{1}H NMR ($DCCl_3$) δ 0.92 [s, 3 H, CH_3(a)], 1.21 [s, 3 H, CH_3(e)], 6.32 [br s, 1 H, H(4)], 6.75 [d, 1 H, H(2)], 7.26–7.63 [m, 6 H, Ar H and H(1)].

Reduction with Lithium Aluminum Hydride. To a well-stirred slurry of $LiAlH_4$ (1.52 g, 0.04 mol) in dry ether was added dropwise a solution of 4-thianone **3e** (8.46 g, 0.03 mol) in dry ether (110 mL). The mixture was heated under reflux for 6 h. Excess hydride was carefully destroyed by the dropwise addition of ethyl acetate, and the resultant mixture was neutralized with hydrochloric acid (5%, 25 mL) and extracted (ether). The combined extracts were washed with sodium bicarbonate (3%) and water and dried. The crude product, obtained after removal of ether, was subjected to chromatography. Details are given in Tables II and V. Similar conditions were used to reduce the other ketones.

Meerwein–Ponndorf–Verley Reduction. The reduction was carried out in a manner slightly modified from that described in the literature[40] using 0.017 mol of the thianone and 0.035 mol of aluminum isopropoxide. Most of the solvent was removed by distillation under diminished pressure. The residue was treated with hydrochloric acid (5 N, 100 mL) and allowed to stand overnight. A solid separated and was filtered, washed with water, dried, and subjected to column chromatography. Details are furnished in Tables II and V.

Chromatographic Separation of the Mixture of Epimeric 4-Thianols. For 1 g of the mixture of alcohols, 30 g of neutral alumina (Merck) was used. Elutions were carried out with petroleum ether (bp 60–80 °C), petroleum ether–benzene (1:1), benzene, benzene–ether (1:1), and ether in the order given. Fractions (5) of 25 mL were collected for each eluent. The solvent was removed on a water bath, and the yield and melting point of each solid from each fraction were determined. The fractions melting at the same temperature were collected and purified either by crystallization from suitable solvents or by rechromatography. The axial alcohols were obtained from the petroleum ether–benzene and benzene eluates and the equatorial alcohols from the benzene–ether and ether eluates.

Preparation of the Sulfones. Hydrogen peroxide solution (30%, 5 mL) was added dropwise to a solution of the cyclic sulfide **3c** (1 g, 0.0034 mol) in acetic acid (10 mL) until the solution became slightly turbid. The reaction mixture was left at room temperature for 72 h and was poured onto crushed ice. The precipitated sulfone **5a** was collected, washed with water, dried, and recrystallized from a suitable solvent. The details are given in Tables III and IV. This general procedure was used for the other compounds.

Acetyl Derivatives of the 4-Thianols. A solution of the 4-thianol **7b** (0.42 g, 0.0015 mol) in dry pyridine (5 mL) was treated with acetic anhydride (1.5 g, 0.015 mol). The reaction mixture was heated on a steam bath for 5 h and poured over crushed ice. The acetate obtained was crystallized from a suitable solvent. Other relevant data are given in Tables II and IV. This was the general procedure employed.

***cis*-2,6-Diphenyl-3,3,5,5-tetradeuterio-4-thianone (10a).** To a mixture of **3a** (5.36 g, 0.02 mol) and 90 g (4.5 mol) of deuterium oxide (99.9%) was added anhydrous sodium carbonate (2.65 g, 0.025 mol), and the mixture was boiled with stirring under N_2 for 24 h. Upon cooling, a solid separated and was filtered, washed with water, and dried. Recrystallization (ethanol) gave 4.8 g (89.5%) of **10a**: mp 111–112 °C; IR (KBr) 1701 cm^{-1} (C=O); ^{1}H NMR ($DCCl_3$) δ 4.29 [s, 2 H, H(2), H(6)], 7.24–7.40 (m, 10 H, Ar H); mass spectrum, m/e (rel intensity) 272 (M^+, 33).

2,2-Dimethyl-6-phenyl-3,3,5,5-tetradeuterio-4-thianone (10c). 2,2-Dimethyl-6-phenyl-4-thianone (**3e**) was converted to **10c** (85%) as described above for **10a**: mp 45–46 °C; IR (KBr) 1698 cm^{-1} (C=O); ^{1}H NMR ($DCCl_3$) δ 4.29 [s, 1 H, H(6)], 1.39 [s, 3 H, CH_3(a)], 1.42 (s, 3 H, CH_3(e)], 7.24–7.42 (m, 5 H, Ar H); mass spectrum, m/e 224 (M^+).

***r*-2,*cis*-6-Diphenyl-*trans*-3-methyl-3,3,5-trideuterio-4-thianone (10b).** Thianone **3c** (5.64 g, 0.02 mol) was placed in a 100-mL, round-bottom flask fitted with a condenser and an N_2 inlet. Deuterium oxide (90 g, 4.25 mol) and sodium deuteroxide in deuterium oxide (40%, 0.1 mL) were added to the flask, and the mixture was heated at 70 °C for 24 h. After the reaction was complete, the contents were cooled and **10b** was filtered off, dried, and recrystallized from petroleum ether (60–80 °C): yield 76%; mp 124–125 °C; IR (KBr) 1702 cm^{-1} (C=O); ^{1}H NMR ($DCCl_3$) δ 0.9 (s, 3 H, CH_3), 3.92 [s, 1 H, H(2)], 4.32 [s, 1 H, H(6)], 7.24–7.41 (m, 10 H, Ar H); mass spectrum, m/e 285 (M^+).

***cis*-2,6-Diphenyl-3,3,5,5-tetradeuteriothian-*r*-4-ol (11a).** This compound was obtained by $LiAlH_4$ reduction of **10a** in ether. Recrystallization (ethanol) gave a solid: yield 92%; mp 154–155 °C; IR (KBr) 1054 cm^{-1} (HC–OH); ^{1}H NMR ($DCCl_3$) δ 1.96 (s, 1 H, OH), 3.74 [s, 1 H, H(4)], 4.06 [s, 2 H, H(2), H(6)]. The reported melting point for the nondeuterated compound was 149–150 °C.[19]

***cis*-2,*trans*-6-Diphenyl-3,3,5,5-tetradeuteriothian-*r*-4-ol (12a).** L-SELECTRIDE (lithium tri-*sec*-butylborohydride, Aldrich Chemical Co.) (10 mL, 1.0 M THF) was cooled to −78 °C, and a solution of **10a** (1 g, 0.0036 mol; preparation is given above) in THF (15 mL) was added slowly with stirring for 3 h. After the addition of 6 mL of 3 N NaOH, the mixture was warmed to room temperature and 3 mL of 30% H_2O_2 was added. The mixture was stirred at room temperature for 15 min. The alkaline mixture was neutralized with 15 mL of 3 N HCl and extracted with ether (3 × 25 mL). The organic layer was washed with water and brine and dried (Na_2SO_4). Removal of solvent gave crude alcohol (0.9 g) that was chromatographed over neutral alumina (25 g). The axial alcohol **12a** (0.78 g, 77.5%) was obtained from ether–benzene eluates. The alcohol **12a** was recrystallized from petroleum ether (60–80 °C): mp 139–140 °C; IR (KBr) 1033 cm^{-1} (HC–OH); ^{1}H NMR ($DCCl_3$) δ 1.70 (s, 1 H, OH), 4.43 [s, 1 H, H(4)], 4.54 [s, 2 H, H(2), H(6)], 7.20–7.42 (m, 10 H, Ar H). The reported melting point for the nondeuterated compound was 139–140 °C.[19]

Lithium Aluminum Hydride Reduction of 2,2-Dimethyl-6-phenyl-3,3,5,5-tetradeuterio-4-thianone (10c). Ketone **10c** was reduced by $LiAlH_4$ in ether to a mixture of alcohols in 90% yield. This product was chromatographed over alumina. The petroleum ether–benzene fractions gave the alcohol **12c** (47%): mp 65–66 °C (from aqueous ethanol); IR (KBr) 1040 and 1018 cm^{-1} (HC–OH); ^{1}H NMR ($DCCl_3$) δ 1.54 (s, 1 H, OH), 1.67 [s, 3 H, CH_3(a)], 1.25 [s, 3 H, CH_3(e)], 4.39 [s, 2 H, H(4), H(6)], 7.20–7.50 (m, 5 H, Ar H). The equatorial alcohol **11c** was obtained (45%) from benzene, benzene–ether eluates. It was crystallized (ethanol): mp 92–93 °C; IR (KBr) 1041 cm^{-1} (HC–OH); ^{1}H NMR ($DCCl_3$) δ 1.96 (s, 1 H, OH), 3.74 [s, 1 H, H(4)], 4.06 [s, 1 H, H(6)], 7.20–7.40 (m, 5 H, Ar H). The nondeuterated counterparts are **8d** and **7d** respectively.

Lithium Aluminum Hydride Reduction of *r*-2,*cis*-6-Diphenyl-*trans*-3-methyl-3,5,5-trideuterio-4-thianone (10b). Reduction of **10b** (2.38 g, 0.008 mol) with $LiAlH_4$ (0.5 g, 0.013 mol) in ether (110 mL) afforded a mixture (2.34 g, 97%) of alcohols **11b** and **12b**. The alcohols could be separated by column chromatography over alumina (70 g) to give **11b** (0.84 g, 35%) and **12b** (0.45 g, 19%). The equatorial alcohol **11b** was recrystallized (aqueous ethanol): mp 154–155 °C; IR (KBr) 1025 cm^{-1} (CH–OH); ^{1}H NMR ($DCCl_3$) δ 1.9 (s, 1 H, OH), 0.92 (s, 3 H, CH_3), 3.45 [s, 1 H, H(4)], 3.76 [s, 1 H, H(6)], 4.13 [s, 1 H, H(2)], 7.20–7.48 (m, 10 H, Ar H). The axial isomer **12b** was crystallized (aqueous ethanol): mp 157–158 °C; IR (KBr) 990 cm^{-1} (CH–OH); ^{1}H NMR ($DCCl_3$) δ 1.73 (s, 1 H, OH), 4.16 [s, 1 H, H(4)], 4.21 [s, 1 H, H(6)], 4.58 [s, 1 H, H(2)], 7.18–7.50 (m, 10 H, Ar H).

Meerwein–Ponndorf–Verley Equilibration of 8a–d. Into a 250-mL, round-bottom flask were placed 1 g (0.0035 mol) of axial alcohol **8b**, 5 g (0.025 mol) of aluminum isopropoxide, 75 mL of isopropyl alcohol, and 2 mL of anhydrous acetone. The mixture was heated under reflux for 140 h. Chromatographic analysis of the hydrolyzed mixture showed the presence of equatorial alcohol **7b** almost exclusively and only a trace of axial alcohol **8b**.

Crystallographic Experimental Data. A summary of crystallographic data has been compiled in Table VII. The crystals used were grown from appropriate solvents (see Table VII). The unit cell parameters were determined by a least-squares fit to the +2θ and −2θ values of 48 reflections distributed through all octants of reciprocal

Table VII. Crystallographic Data

	4b	4c
formula	$C_{18}H_{18}OS$	$C_{19}H_{20}OS$
fw	282.18	296.21
space group	*Iba*2	*Iba*2
systematic extinctions		
hkl	$h + k + l \neq 2n$	$h + k + l \neq 2n$
0*kl*	$k \neq 2n$	$k \neq 2n$
*h*0*l*	$h \neq 2n$	$h \neq 2n$
a	39.389 (1) Å	39.414 (2) Å
b	10.5224 (5) Å	10.8315 (5) Å
c	7.1062 (3) Å	7.3941 (3) Å
V	2945.3 $Å^3$	3156.6 $Å^3$
Z	8	8
radiation (Cu $K\alpha_1$)	1.54051 Å	1.54051 Å
density (calcd)	1.272 g cm^{-3}	1.246 g cm^{-3}
μ (Cu $K\alpha$)	18.22 cm^{-1}	17.24 cm^{-1}
solvent for crystallization	acetone	acetonitrile
crystal dimensions	0.19 × 0.59 × 0.62 mm	0.11 × 0.34 × 0.50 mm

space. A summary of data collection and structure refinement values is listed in Table VIII. Intensity data were measured on a Nonius CAD-4 automatic diffractometer with θ–2θ scan techniques utilizing a variable scan width calculated as $(0.9 + 0.09 \tan \theta)°$ for each reflection. A receiving aperature with variable width $(5.7 + 0.86 \tan \theta)°$ and a constant height of 6 mm was located 173 mm from the crystal. A reflection was scanned for a maximum time of 90 s with two-thirds of that time spent scanning the peak (*P*) and one-sixth of the time spent scanning each the left and right backgrounds (*LB* and *RB*). The unscaled intensity was calculated as $I = P - 2(LB + RB)$. The scan time was less than 90 s for those intensities where a value of 40 000 for *I* could be attained with a faster scan speed than the base 1.1°/min. A monitor reflection was measured after every 25 reflections. Overall changes in the intensity of the monitor reflections were less than 2%.

Three orientation control reflections were centered after every 100 measurements. In the case that any of the θ, ω, ϕ, or κ angles of these reflections changed 0.1°, a new orientation matrix was automatically determined from a list of 11 reflections. Reflections having $I \leq 2\sigma(I)$ were considered indistinguishable from background and were assigned an intensity equal to $1.4 \times T^{1/2}$ ($T = P + 2LB + 2RB$) for the purpose of least-squares refinement. A Gaussian method[41] was employed to make the absorption correction by using 216 sampling points. Each structure factor was assigned a weight given by $w_F = 1/\sigma_F^2$, where σ_F is defined as in eq 1; $\sigma = (T^{1/2})\nu$, ν is the scan speed, and Lp is the Lorentz–polarization factor. The program MULTAN was used for the structure solution of **4b**; isomorphism was assumed for **4c** and was used for that structure solution.

$$\sigma_F = \frac{1}{2}\left[\frac{\sigma^2 + (0.04I\nu)^2}{(\mathrm{Lp})(I\nu)}\right]^{1/2} \quad (1)$$

The atomic positions, temperature factors, and scale factor were refined with the full-matrix structure factor least-squares program ORFLS,[42] in which the quantity $\Sigma w_f||F_o| - |kF_c||^2$ was refined. Most hydrogen atoms were readily located from difference Fourier synthesis and included in the refinement. The remaining hydrogen atoms either were given idealized positions or were not included in the structure factor calculation. In the last stages of refinement, the anomalous scattering of sulfur and oxygen was taken into account. Because the compounds crystallized in a polar space group (*Iba*2), the anomalous scattering allowed the determination of the polarity. The correct polarity was determined by refining two sets of atomic parameters for both **4b** and **4c**. Least-squares refinement of atomic parameters was terminated when all shifts were small fractions of the corresponding standard deviations. The two sets of parameters for **4b** refined to *R*− values of 0.060 and 0.063 and for **4c** to 0.058 and 0.61, and it was therefore possible to ascertain the correct polarity for each compound as the one with the lower residual using the *R*− method of Hamilton.[43] The scattering factors for S, O, and C atoms were taken from the "International Tables for X-Ray Crystallography"[44] and those for H atoms from Stewart, Davidson, and Simpson.[45] The *R*− values were based on all data and final parameters (Tables IX and X of supplementary material[46]).

Table VIII. Data Collection and Structure Refinement Parameters

	4b	4c
diffractometer	Nonius CAD-4	Nonius CAD-4
radiation (Cu $K\bar{\alpha}$)	1.5418 Å	1.5418 Å
data limits	$2° \leq 2\theta \leq 150°$	$2° \leq 2\theta \leq 150°$
maximum scan	90 s	90 s
scan type	θ–2θ	θ–2θ
no. of reflections	1650	1757
no. of observed reflections	1617	1679
method of solution	MULTAN	isomorphism
method of refinement	least-squares	least-squares
final *R* value	0.060	0.058
greatest residual density in final difference Fourier	0.6 e/$Å^3$	0.5 e/$Å^3$
final shifts	$<1\sigma$	$<1\sigma$

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Registry No.—**1a**, 3152-68-9; **1b**, 4646-80-4; **2c**, 14164-67-7; **2d**, 63114-78-3; **2e**, 55901-61-6; **3b**, 68226-73-3; **3c**, 68226-04-0; **3c** semicarbazone, 68226-74-4; **3c** oxime, 68226-75-5; **3d**, 68226-05-1; **3d** oxime, 68226-76-6; **3d** semicarbazone, 68226-77-7; **3e**, 68226-11-9; **3e** oxime, 68226-78-8; **3e** semicarbazone, 68226-79-9; **4b**, 68296-29-7; **4b** oxime, 68331-90-8; **4c**, 68296-30-0; **4c** oxime, 68296-56-0; **5a**, 68226-66-4; **5b**, 68226-67-5; **6a**, 68366-06-3; **6b**, 68296-46-8; **7a**, 68296-34-4; **7b**, 68226-14-2; **7c**, 68226-23-3; **7d**, 68226-24-4; **7e**, 68226-68-6; **7f**, 68226-69-7; **7g**, 68226-70-0; **7h**, 68226-64-2; **7i**, 68226-65-3; **7j**, 68226-71-1; **7k**, 68226-72-2; **8a**, 68296-35-5; **8b**, 68296-31-1; **8c**, 68296-37-7; **8d**, 68226-25-5; **8e**, 68296-47-9; **8f**, 68296-48-0; **8g**, 68296-49-1; **8h**, 68296-42-4; **8i**, 68296-43-5; **8j**, 68296-50-4; **8k**, 68296-51-5; **9a**, 68296-39-9; **9b**, 68296-40-2; **9c**, 68296-52-6; **9d**, 68296-53-7; **9e**, 68296-44-6; **9f**, 68296-45-7; **9g**, 68296-54-8; **9h**, 68296-55-9; **10a**, 68226-15-3; **10b**, 68226-16-4; **10c**, 68226-17-5; **10d**, 68226-80-2; **11a**, 68226-19-7; **11b**, 68226-20-0; **11c**, 68226-21-1; **12b**, 68296-33-3; **12c**, 68226-22-2; **12d**, 68296-57-1; benzaldehyde, 100-52-7; H_2S, 7783-06-4; mesityl oxide, 141-79-7; deuterium oxide, 7789-20-0.

Supplementary Material Available: Final nonhydrogen atomic positional parameters for **4b** and **4c**, Tables IX and X (2 pages). Ordering information is given on any current masthead page.

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Formation and Synthetic Utility of Dihydro- and Dihydrothiapyrans[1]

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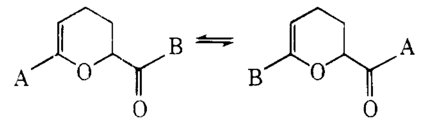
The utility of the Diels–Alder reaction to form 2,3-dihydropyran derivatives and the subsequent incorporation of other functionality by Cope rearrangement have been studied. Brevicomin, the aggregating sex pheromone for *Dendroctonus brevicomis*, has been synthesized, and the mass spectral fragmentation patterns of related bicyclic ketals have been compared. A theoretical prediction of regioselection in the (4 + 2) cycloaddition reactions appears quite consistent with experimental observation, particularly for heterodienes containing sulfur.

The molecular rearrangement of dihydropyran 1 to 2 was first investigated by Roberts.[2] Since then, only Büchi and

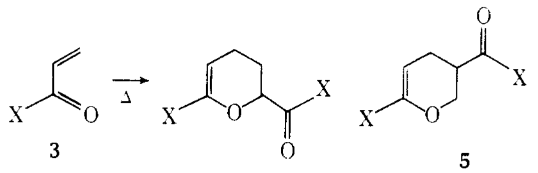


1 2

Powell have taken advantage of this [3,3] sigmatropic shift to gain entry into substituted cyclohexene systems.[3] Now we wish to discuss the preparation of these pyranyl systems and their utility as precursors to new compounds. This paper is divided into three sections. Part I discusses theoretical and synthetic aspects of cycloadditions that form dihydropyrans. Included in this section is a new synthesis of brevicomin, the aggregating sex pheromone of the pine bark beetle, *Dendroctonus brevicomis*, and a study of the mass spectral fragmentation patterns of related bicyclic ketals available from dihydropyrans. Part II analyzes the possibility of forming dihydrothiapyrans from either Diels–Alder reactions or Cope rearrangement of substituted dihydropyrans. Part III will focus on our inability to incorporate nitrogen into the molecular framework, and will give details regarding an interesting secondary rearrangement in this work.

Part I

The generation of a suitable ring structure that may be chemically modified before or after rearrangement is a necessity if one is to ensure the generality of a synthetic method. To this end we point out that there may be other routes to dihydropyrans like 1, but here we shall concern ourselves only with the Woodward–Hoffmann allowed (4 + 2) cycloaddition of heterodienes.[4] Usual problems associated with cycloadditions, such as periselectivity and site selectivity, are of no concern to us in this work. Equation 1 reveals, however, that two possible regioisomers, 4 and 5, may form upon dimerization of enone 3. In fact, the synthesis of several natural products critically hinges upon the regioselectivity of these cycloadditions, and considerable interest has been expressed in describing the origin of this selectivity.[5]



3 4 5 (1)