79%). Fraction 1 showed a small infrared peak at 1720 cm^{-1} but no OH absorption; fraction 2 showed a small, broad OH peak at 3500 cm^{-1} but no carbonyl absorption. Both fractions had a terpene-like aroma. Both showed complex ^1H NMR spectra: δ 0.9 (t, J = 7 Hz, CH_3CH_2), 1.2 (d, J = 3 Hz, 4-CH_3), 1.3 (s, 2-CH_3), 1.6 (br q, J = 7 Hz, CH_3CH_2), complex multiplets at 3.3 and 4.0 assigned to the ring protons (C-4 and C-5). The ratio of high-field to low-field integrals was 3.25 for fraction 1 and 3.58 for fraction 2 (calcd, 11/3 = 3.67).

Procedure for Kinetics. Except for the very first exploratory experiments, all solutions were prepared by weighing to $\pm 1 \times 10^{-4}$ g. At first, reagents were weighed directly into quartz cuvettes (1 cm square, capacity ca. 2.5 mL), but the viscosity of propanediol and the relatively small air space hindered mixing and may have been the cause of unsatisfactory precision (±5% or more). For prevention of another conceivable mixing problem, cuvettes were used only if their caps fitted flush with the inside of the cuvette.

Solutions were prepared in 10- or 25-mL, round-bottomed flasks, weighing in first the diol and then the acid, stoppering, and swirling for at least 10 min. The solution was divided equally between two cuvettes, and these were stoppered and allowed to equilibrate for at least 1 h in the thermostated cuvette compartment of the spectrophotometer. For each run, each cuvette was briefly withdrawn, 1 drop of ketone was added, and the cuvette was again tightly stoppered, shaken for ca. 1 min, and replaced in the compartment. Measurement was begun as soon as all cuvettes were ready.

Absorbances were measured via a Beckman automatic recording spectrophotometer. With the wavelength set at 280 nm, the instrument moved each cuvette into the sample beam for a chosen dwell time, usually 15–20 s, and repeated the cycle of measurements over a chosen interval, usually 1.5–2 min in this work. The absorbance of each cuvette at each time appeared as a dot on the chart. Measurements were continued until A for each cuvette had become constant. The absorbance of each cuvette was monitored for at least 30 min prior to addition of ketone. Absorbances were treated as described in the Results and Discussion, rate constants being determined graphically.

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Registry No. (*S*)-(−)-Ethyl *O*-acetyllactate, 20918-91-6; (*S*)-(−)-ethyl lactate, 687-47-8; (*S*)-(+)-1,2-propanediol, 4254-15-3; (±)-1,2-propanediol, 4254-16-4; (±)-1,2-propanediol-*O*,*O*-d_2, 77080-53-6; 2-ethyl-2,4-dimethyl-1,3-dioxolane, 2916-28-1; butanone, 78-93-3.

Studies on the Conformation of Some Substituted 4-Selenanols

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The second-order rate constants for acetylation with acetic anhydride in pyridine have been measured at 40 °C for seven pairs of epimeric 4-selenanols, and the conformations of these compounds were determined from the kinetic data. ^1H NMR and ^{13}C NMR spectra were also recorded and analyzed. The ^1H chemical shift of the carbinol protons and ^{13}C chemical shift of the carbinol carbons are analyzed in the light of previously established correlations. Carbon-13 chemical shift data suggest that 2,2-dimethyl-*trans*-6-(*p*-chlorophenyl)selenan-*r*-4-ol exists in a nonchair conformation.

The kinetics of acetylation of epimeric alcohols[2-4] has been one of the well-devised methods to elicit corroborative evidence concerning the configuration of the hydroxyl group. Although the rates of acetylation of 4-piperidinols[5] and 4-thianols[6] are on record, no systematic investigation of a series of 4-selenanols has appeared nor have there been many studies[7] of the conformational analysis of functionalized selenium heterocycles. We report a conformational study of some epimeric pairs of substituted 4-selenanols based on the rates of acetylation as well as ^1H and ^{13}C NMR spectral analysis.

Table I. Composition of the Products from the Reduction of 4-Selenanones

selenanone	% total crude product	% unreduced selenanone	yield of epimeric selenanols, % axial	equatorial
	Reduction with MPV			
5a	98	3	63 (1a)	15 (2a)
5b	96	4	53 (1c)	15 (2c)
5c	93	4	75 (3b)	14 (4b)
	Reduction with $LiAlH_4$			
5a	98	3	11	84
5b	97	4	12	68
5c	96	3	47	44

(1) Taken in part from the Ph.D. Thesis of P.N. to be submitted to the University of Madras, India.
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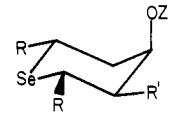
0022-3263/81/1946-2542$01.25/0

Table II. Substituted 4-Selenanols and Corresponding Acetates

compd	yield, %	mp, °C	formula	analysis: % found C	% found H	% calcd C	% calcd H
1a	*e*	131-132[d]	$C_{17}H_{18}OSe$	64.28	5.69	64.35	5.72
1c	*e*	166-167[a]	$C_{19}H_{22}O_3Se$	60.40	5.91	60.48	5.88
1f	80	171-172[a]	$C_{19}H_{20}O_2Se$	63.45	5.64	63.51	5.61
1g	72	149-150[b]	$C_{21}H_{24}O_4Se$	60.21	5.75	60.14	5.77
2a	*e*	183-184[a]	$C_{17}H_{18}OSe$	64.26	5.75	64.35	5.72
2c	*e*	193-194[a]	$C_{19}H_{22}O_3Se$	60.53	5.84	60.48	5.88
2f	81	143-144[a]	$C_{19}H_{20}O_2Se$	63.62	5.59	63.59	5.61
2g	77	160-161[a]	$C_{21}H_{24}O_4Se$	60.03	5.80	60.14	5.77
3b	*e*	75-76[c]	$C_{13}H_{17}OSeCl$	51.32	5.60	51.41	5.64
3c	73	66-67[c]	$C_{15}H_{19}O_2SeCl$	52.20	5.56	52.11	5.54
4b	*e*	105-106[c]	$C_{13}H_{17}OSeCl$	51.36	5.61	51.41	5.64
4c	70	121-122[c]	$C_{15}H_{19}O_2SeCl$	52.02	5.51	52.11	5.54

[a] Recrystallized from ethanol. [b] Recrystallized from aqueous ethanol. [c] Recrystallized from petroleum ether (bp 60-80 °C). [d] Recrystallized from benzene-petroleum ether (bp 60-80 °C). [e] The yields for the selenanols depend upon the reducing conditions (see Table I).

The synthesis and ^1H and ^{13}C NMR spectra of some substituted 4-selenanones and 4-selenanols **1b,d,e, 2b,d,e, 3a**, and **4a** were reported recently from this laboratory.[7]



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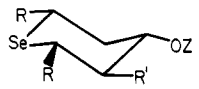
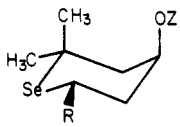


2

	R	R′	Z
a	C_6H_5	H	H
b	C_6H_4-*p*-CH_3	H	H
c	C_6H_4-*p*-OCH_3	H	H
d	C_6H_5	CH_3	H
e	C_6H_5	C_2H_5	H
f	C_6H_5	H	C(O)CH_3
g	C_6H_4-*p*-OCH_3	H	C(O)CH_3



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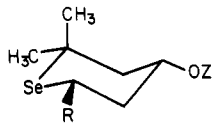
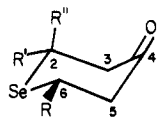


4

	R	Z
a	C_6H_5	H
b	C_6H_4-*p*-Cl	H
c	C_6H_4-*p*-Cl	C(O)CH_3

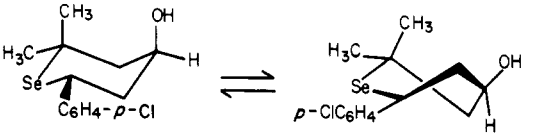
Epimeric 4-selenanols **1a, 2a, 1c, 2c, 3b**, and **4b** were prepared from reduction of the corresponding 4-selenanones **5a-c**, respectively, by lithium aluminum hydride in ether and aluminum isopropoxide in isopropyl alcohol and were separated by column chromatography over neutral alumina. The results are recorded in Tables I and II.



5

	R	R′	R″
a	C_6H_5	C_6H_5	H
b	C_6H_4-*p*-OCH_3	C_6H_4-*p*-OCH_3	H
c	C_6H_4-*p*-Cl	CH_3	CH_3

The configuration of 4-selenanols **1a, 2a, 1c, 2c, 3b**, and **4b** is assigned on the basis of ^1H NMR and ^{13}C NMR spectral data which are summarized in Tables III and IV. The configuration of the hydroxyl group may be deduced from the chemical shift data of H(4). The H(4) protons attached to the equatorial C(4)-OH bonds of the 4-selenanols are shielded to a greater extent than the H(4) protons of the axial epimer. It can be seen from Table III that the half-width signals[8] for H(4) for the 4-selenanols **1a** and **1c** [axial C(4)-OH bond] are 10.0 and 9.0 Hz (smaller), respectively, as compared to 19.5 and 19.0 Hz (larger) for the corresponding equatorial epimers **2a** and **2c** [equatorial C(4)-OH bond]. The half-width of the H(4) proton signal for 4-selenanol **4b** is 20.50 Hz, confirming that the hydroxyl function is equatorial whereas in its epimer **3b** the corresponding value is 12.0 Hz. This latter value is somewhat larger than the $w_{1/2}$ of the H(4) protons of axial 4-selenanols **1a** and **1c**. The broadness of the peak, 12.0 Hz at half-height, is indicative of a possible nonchair conformation for **3b** wherein the syn diaxial (CH_3···OH) interaction can be relieved to some extent. The hydroxyl group may acquire a pseudoequatorial orientation in the nonchair conformation which would explain the larger $w_{1/2}$ value (12.0 Hz). Detailed information regarding the conformation of 4-selenanol **3b** can be obtained by the analysis of the signal at δ 4.53 (t, J = 7.0 Hz, dd merged into a t) which corresponds to H(6). This proton in the parent ketone **5c** appears as a doublet of doublets (J = 11.0 and 4.0 Hz). The coupling constants which are typical for vicinal coupling constants J_{anti} and J_{gauche} in the chair conformation in cyclohexyl systems suggest that the parent ketone is in the regular chair conformation. Thus, in contrast, the ^1H NMR data of **3b** suggest a possible twist conformation **3b′**.



3b 3b′

Such a view is also supported by carbon-13 chemical shift data on **3b**. As corroborative evidence, the $w_{1/2}$ values for H(4) in **3a** and **4a** were 12.0 and 20.5 Hz, respectively. Again for H(6) in **3a**, the signal appeared as a triplet (δ 4.56, J = 7.5 Hz) rather than an expected doublet of doublets.[7]

The configuration assigned to the 4-selenanols was also supported by the ^{13}C chemical shift data. Examination

(8) For a general review of the significance of $w_{1/2}$ in assigning the signals from an axial or equatorial C-H bonds, see: Jackman, L. M.; Sternhell, S. "Applications of NMR Spectroscopy in Organic Chemistry", 2nd ed.; Pergaman Press: Oxford, 1969; Chapters 1,2.

Table III. ^{1}H NMR Data[a] for Substituted 4-Selenanols and the Corresponding Acetates

compd	chemical shift					
	H(2)	H(3)	H(4)	H(5)	H(6)	other
1a	4.82 [2 H, H(2), H(6), dd merged into t, J = 8.0 Hz]	2.02-2.52 [m, 5 H, H(3), H(5), OH]	4.43 (br s, $w_{1/2}$ = 10.0 Hz)	overlapped with H(3)	overlapped with H(2)	OH overlapped with H(3) and H(5), 7.00-7.54 (m, 10 H Ar H)
1c	4.77 [dd, 2 H, H(2), H(6), J = 10.0, 4.0 Hz]	2.26-2.48 [m, 4 H, H(3), H(5)]	4.46-4.64 (m, $w_{1/2}$ = 9.0 Hz)			1.73 (s, 1 H, OH), 3.76 (s, 6 H, OCH_3), 6.74-6.92 (m, 4 H, Ar H), 7.20-7.40 (m, 4 H, Ar H)
1f	4.66 [dd, 2 H, H(2), H(6), J = 11.25, 3.0 Hz]	2.26-2.62 [m, 4 H, H(3), H(5)]	5.50 (br s, $w_{1/2}$ = 9.0 Hz)			2.06 (s, 3 H, $COCH_3$), 7.03-7.45 (m, 10 H, Ar H)
1g	4.65 [dd, 2 H, H(2), H(6), J = 11.75, 3.5 Hz]	2.24-2.68 [m, 4 H, H(3), H(5)]	5.54 (br s, $w_{1/2}$ = 11.5 Hz)			2.11 (s, 3 H, $COCH_3$), 3.70 (s, 6 H, OCH_3), 6.70-6.95 (m, 4 H, Ar H), 7.16-7.40 (m, 4 H, Ar H)
2a	4.50 [dd, 2 H, H(2), H(6), J = 12.0, 3.0 Hz]	1.76-2.74 [m, 4 H, H(3), H(5)]	3.58-4.00 (m, $w_{1/2}$ = 19.5 Hz)			1.64 (s, 1 H, OH), 7.18-7.52 (m, 10 H, Ar H)
2c	4.45 [dd, 2 H, H(2), H(6), J = 12.0, 3.0 Hz]	1.94-2.40 [m, 4 H, H(3), H(5)]	2.44-2.74 (m, $w_{1/2}$ = 19.0 Hz)			1.58 (s, 1 H, OH), 3.77 (s, 6 H, OCH_3), 6.77-6.98 (m, 4 H, Ar H), 7.22-7.41 (m, 4 H, Ar H)
2f	4.45 [dd, 2 H, H(2), H(6), J = 12.0, 3.0 Hz]	2.16-2.72 [m, 4 H, H(3), H(5)]	4.77-5.12 (m, $w_{1/2}$ = 20.0 Hz)			2.00 (s, 3 H, $COCH_3$), 7.06-7.46 (m, 10 H, Ar H)
2g	4.38 [dd, 2 H, H(2), H(6), J = 12.0, 3.0 Hz]	2.14-2.68 [m, 4 H, H(3), H(5)]	4.72-5.10 (m, $w_{1/2}$ = 21.0 Hz)			2.01 (s, 3 H, $COCH_3$), 3.70 (s, 6 H, OCH_3), 6.70-6.94 (m, 4 H, Ar H), 7.16-7.39 (m, 4 H, Ar H)
3b		1.93 (d, J = 4.0 Hz)	4.40 (br s, $w_{1/2}$ = 12.0 Hz)	2.12-2.37 (m)	4.53 (t, J = 7.0 Hz, dd merged into into t)	1.32 (s, 3 H, CH_{3a}), 1.78 (s, 3 H, CH_{3e}), 2.04 (s, 1 H, OH), 7.02 (s, 4 H, Ar H)
3c		1.95 (d, J = 3.5 Hz)	5.32-5.52 (m, $w_{1/2}$ = 11.0 Hz)	2.21-2.42 (m)	4.48 (dd, J = 10.0, 4.0 Hz)	1.34 (s, 3 H, CH_{3a}), 1.72 (s, 3 H, CH_{3e}), 2.06 (s, 3 H, $COCH_3$), 7.25 (s, 4 H, Ar H)
4b		1.80-2.16 (m)	3.67-4.06 (m, $w_{1/2}$ = 20.5 Hz)	2.27-2.66	4.20 (dd, J = 12.0, 3.0 Hz)	1.39 (s, 3 H, CH_{3a}), 1.58 (s, 3 H, CH_{3e}), 1.74 (s, 1 H, OH), 7.21 (s, 4 H, Ar H)
4c		1.82-2.19 (m)	4.48-5.24 (m, $w_{1/2}$ = 22.0 Hz)	1.94-2.26 (m), 2.34-2.63 (m)	4.30 (dd, J = 13.5, 3.5 Hz)	1.41 (s, 3 H, CH_{3a}), 1.67 (s, 3 H, CH_{3e}), 2.03 (s, 3 H, OCH_3), 7.24 (s, 4 H, Ar H)

[a] NMR shifts are in δ units. Abbreviations used: s, singlet; d, doublet; dd, doublet of doublets; t, triplet; m, multiplet; br s, broad singlet.

of the data in Table IV indicates that shielding of the carbinol carbon C(4) is greatly affected by the configuration of the hydroxyl function; an axial hydroxyl group shields this carbon by about 4–5 ppm. Such chemical shift differences for 4-piperidinols, 4-thianols, and 4-oxanols have been clearly established.[9] It is also interesting to compare the C(4) chemical shift data of the epimeric pairs of 2,2-dimethyl-6-(*p*-chlorophenyl)-4-selenanols **3b** and **4b** which are very similar. The upfield shift (68.47 ppm) of C(4) (equatorial hydroxyl group) in **4b** compared to the C(4) resonance (72.10 ppm) in **2a** is probably due to steric interaction of the axial methyl group. From this observation one would be tempted to expect a larger upfield shift for C(4) in **3b** relative to that found for C(4) in **4b**. Surprisingly, the chemical shift (68.47 ppm) of C(4) in the equatorial epimer **4b** is not very much lower than the chemical shift (68.20 ppm) of the axial epimer **3b**. This could lead to the speculation that in the equilibrium shown

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(10) Whol, R. A. *Chemia* **1964**, *18*, 219.

Table IV. ^{13}C Chemical Shifts of Substituted 4-Selenanols and the Corresponding Acetates

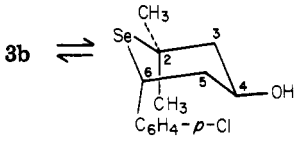
compd[a]	chemical shift, δ C(2)	C(3)	C(4)	C(5)	C(6)	other
1a	35.49	39.86	67.12			Ar, 141.91, 128.46, 127.38, 127.01
1c	34.73	40.19	67.41			OCH_3, 55.15; Ar, 158.31, 134.12, 128.34, 113.81
1f	36.01	37.01	69.98			$COCH_3$, 21.21; C=O, 169.51; Ar, 141.26, 128.40, 127.17, 127.08
1g	35.37	37.26	70.15			$COCH_3$, 21.21; C=O, 169.57; OCH_3, 55.06; Ar, 158.42, 133.44, 128.19; 113.81
2a	40.91	43.63	72.10			Ar, 141.06, 128.49, 127.17
2c	40.21	43.92	72.19			OCH_3, 55.18; Ar, 158.48, 133.27, 128.19, 113.87
3b	40.38	47.13	68.20	39.45	33.10	CH_{3a}, 31.93; CH_{3e}, 32.89; Ar, 140.74, 132.13, 128.74, 128.31
3c	38.84	43.92	70.68	37.47	32.37	$COCH_3$, 21.27; C=O, 169.52; CH_{3a}, 32.42; CH_{3e}, 32.83; Ar, 140.24, 132.37, 128.69, 128.40
2f	40.07	40.27	73.27			$COCH_3$, 21.10; C=O, 169.54; Ar, 140.74, 128.40, 127.14, 127.06
2g	39.63	40.36	73.77			$COCH_3$, 21.16; C=O, 169.54; OCH_3, 55.04; Ar, 158.49, 132.98, 128.11, 113.84
4b	43.98	51.48	68.47	41.12	36.92	CH_{3a}, 30.70; CH_{3e}, 32.01; Ar, 139.76, 132.46, 128.52, 128.46
4c	40.45	47.62	70.91	40.22	36.33	$COCH_3$, 21.10; C=O, 169.60; CH_{3a}, 30.41; CH_{3e}, 31.84; Ar, 139.45, 132.48, 128.46, 128.39

[a] All data are given in parts per million downfield from Me_4Si; the solutions used were 0.3 M in $DCCl_3$.

Table V. Second-Order Rate Constants of the Acetylation of 4-Selenanols with Acetic Anhydride in Pyridine at 40 °C

compd	10^5k, L mol^{-1} s^{-1}	compd	10^5k, L mol^{-1} s^{-1}	k_e/k_a
1a	16.49 ± 0.22	2a	45.66 ± 0.33	2.77
1b	16.91 ± 0.10	2b	47.24 ± 0.17	2.79
1c	16.17 ± 0.08	2c	44.81 ± 0.14	2.77
1d	7.83 ± 0.15	2d	52.50 ± 0.24	6.71
1e	4.52 ± 0.02	2e	60.52 ± 0.34	13.39
3a	7.47 ± 0.06	4a	33.20 ± 0.03	4.44
3b	7.30 ± 0.06	4b	32.20 ± 0.29	4.41

the conformer with an axial hydroxyl group is in very small population and the compound predominantly exists as **3b″**.



3b″

The syn diaxial CH_3···C_6H_4-*p*-Cl interaction in **3b″** should be severe enough, however, to destabilize a chair conformation. Consequently, the chair form should be severely distorted, or the compound should prefer a nonchair conformation. ^1H NMR spectral studies also lead to the similar conclusion regarding the major conformation of **3b** in solution.

In the present investigation the rates of acetylation of a number of epimeric pairs of substituted 4-selenanols were determined at 40 °C by using acetic anhydride in pyridine. Essentially, the procedure of Eliel and Biros[3] was followed. The acetylation rates are listed in Table V.

cis-2,*cis*-6-Diphenylselenan-*r*-4-ol (**2a**) is three times as reactive as *trans*-2,*trans*-6-diphenylselenan-*r*-4-ol (**1a**). This difference in rate as well as the large size of the phenyl groups suggests that these compounds are likely conformationally biased. The very similar rate constants for the acetylation of *cis*-2,*cis*-6-diphenylselenan-*r*-4-ol (**2a**), *cis*-2,*cis*-6-di-*p*-tolylselenan-*r*-4-ol (**2b**), and *cis*-2,*cis*-6-di-*p*-anisylselenen-*r*-4-ol (**2c**) were 45.66×10^{-5}, 47.24×10^{-5}, and 44.81×10^{-5} L mol^{-1} s^{-1}, respectively, and indicate that the group on the phenyl ring does not affect the rate of acetylation appreciably. Isomers **1b** and **1c** [axial C(4)–OH bond] react much more slowly than the equatorially substituted isomers **2b** and **2c**. *cis*-2,*cis*-6-Diphenyl-*trans*-3-methylselenan-*r*-4-ol (**2d**, equatorial C(4)–OH bond) and *cis*-2,*cis*-6-diphenyl-*trans*-3-ethylselenan-*r*-4-ol (**2e**, equatorial C(4)-OH bond) also react much more rapidly than the corresponding epimers **1d** and **1e**. The data in Table V show that the introduction of an alkyl group in the selenanane ring *increases* the rate of acetylation of an equatorial hydroxyl group. This rate-accelerating effect of the alkyl group is probably polar in nature and may be due to the electron-donating effect of the alkyl group. A similar rate-accelerating effect was also found in the rate of acetylation of 2-alkyl-substituted cyclohexanols[8] and 3-alkyl-4-thianols.[6]

In general, an adjacent equatorial alkyl substituent *retards* the rate of acetylation of an *axial hydroxyl group*. As the size of the group increases, its steric effect is manifested in a retardation of the rate of acetylation. The results recorded in Table V show that this is indeed the case for selenanols **1d** and **1e**. It is known that such syn-oriented 1,2-disubstituents are closer to each other than the anti 1,2-disubstituents in six-membered rings.[10] These results are in good agreement with the lower rates of acetylation observed in the case of *cis*-2-alkylcyclohexanols,[3] 3-alkyl-substituted 4-thianols,[6] and 3-alkyl-4-piperidinols.[5] An examination of the rate constants recorded in Table V reveals that the selenanols **4a** and **4b** react 4.5 times faster than their corresponding axial epimers **3a** and **3b**. The rate constant of 2,2-dimethyl-*cis*-6-phenylselenan-*r*-4-ol (**4a**) is considerably lower than that of *cis*-2,*cis*-6-diphenylselenan-*r*-4-ol (**2a**). It is reasonable to assume that an axially placed 2-methyl group will exert little steric or polar effect on the reactivity of an equatorial hydroxyl group provided that the selenanane ring is not distorted. That is, the equatorial isomers **2a**, **4a**, and **4b** in ideal chair conformations should be acetylated more or less at the same rate. However, the rate constants for 2,2-dimethyl-*cis*-6-phenylselenan-*r*-4-ol (**4a**) and 2,2-dimethyl-*cis*-6-(*p*-chlorophenyl)selenan-*r*-4-ol (**4b**) lead us to conclude that the presence of an axial methyl group distorts the regular chair conformation since these rates are drastically lower than in **2a**, for example. The probability of such distortion is greater in the case of axial isomers **3a** and **3b**. These compounds have in the regular chair conformation one CH_3···OH, one OH···H, and one

CH_3···H interaction, amounting to a total repulsive interaction of about 3.7 kcal/mol. Consequently, the chair conformation of the selenanols **3a** and **3b** will be strongly distorted. This conclusion also derives support from the ^1H NMR and ^{13}C chemical shift data for 2,2-dimethyl-*trans*-6-(*p*-chlorophenyl)selenan-*r*-4-ol.

Experimental Section

General Data. Melting points were taken on a BOETIUS hot-stage microscope and are uncorrected. ^1H NMR spectra were obtained on a Varian XL-100(15) high-resolution NMR spectrometer (with a time-averaging computer accessory, C-1024) operating at 100 MHz. The data are expressed in δ values, relative to Me_4Si. Proton-noise-decoupled ^{13}C NMR spectra were recorded at 25.2 MHz on a Varian XL-100(15) NMR spectrometer equipped with a Nicolet TT-100 Fourier transform accessory. Chemical shift data encompassing a 5000-Hz spectral region were collected into 8K data points. Single-frequency, off-resonance spectra were obtained by irradiation with a continuous-wave frequency at about δ −5 compared to Me_4Si in the proton spectrum. The samples were run as 0.3 M solutions in $DCCl_3$ containing tetramethylsilane as an internal reference. The spectra of all samples were recorded at 37 °C. Assignments have been made on the basis of signal multiplicity found in the off-resonance decoupled spectra and from the magnitude of the $^1J_{^{13}C-H}$ couplings.

Preparation of 2,2-Dimethyl-6-(*p*-chlorophenyl)-4-selenanone (5c) and 1-(*p*-Chlorophenyl)-5-methyl-1,4-hexadien-3-one. To a mixture of 4-methyl-3-penten-2-one (30 g, 0.31 mol), *p*-chlorobenzaldehyde (43.6 g, 0.31 mol), hydroquinone (0.3 g), and piperidine (3 mL) was added glacial acetic acid (3 mL), and the mixture was gently boiled for 6 h under N_2. The brown mass obtained was extracted with ether (3 × 200 mL). The ether layer was washed with water followed by a 5% solution of sodium carbonate and was then dried (Na_2SO_4). Evaporation of the ether left a dark brown semisolid which, on fractional distillation, gave 17 g (25%) of 1-(*p*-chlorophenyl)-5-methyl-1,4-hexadien-3-one, bp 155–160 °C (1.7 mm). Purification was achieved by crystallizing the solid in petroleum ether (bp 60–80 °C), mp 92–93 °C. Anal. Calcd for $C_{13}H_{12}OCl$: C, 71.07; H, 5.51. Found: C, 71.14; H, 5.48. To a boiling mixture of 1-(*p*-chlorophenyl)-5-methyl-1,4-hexadien-3-one (5 g, 0.02 mol) and sodium acetate trihydrate (5 g, 0.036 mol) was added aluminum selenide (5 g, 0.017 mol). The reaction mixture was boiled for 6 h, and the ethanol was removed at reduced pressure. Extraction of the residue with hot petroleum ether (bp 60–80 °C, 6 × 20 mL) and removal of the solvent on a rotary evaporator furnished a pale yellow, viscous oil. This oil, in petroleum ether (bp 40–60 °C) and upon refrigeration for 6 h, gave a yellow solid. The solid was collected on a Büchner funnel, washed with ice-cold petroleum ether, and dried to give 4.1 g (60%) of 2,2-dimethyl-6-(*p*-chlorophenyl)-4-selenanone (**5c**): mp 68–69 °C [petroleum ether (bp 40–60 °C)]; ^1H NMR ($DCCl_3$) δ 1.49 (s, 3 H, CH_{3a}), 1.57 (s, 3 H, CH_{3e}), 2.46–3.25 (m, 4 H, H(3), H(5)), 4.52 (dd, 1 H, H(6), J = 11.0 Hz, J = 4.0 Hz), 7.24 (s, 4 H, Ar H); ^{13}C NMR ($DCCl_3$) 30.96 (CH_{3a}), 31.49 (CH_{3e}), 37.53 (C(6)), 42.14 (C(2)), 49.75 (C(5)), 57.93 (C(3)), 138.38, 133.01, 128.69, 128.42 (C–Ar), 208.33 (C(4)) ppm; mass spectrum, m/e 302.0013 (M^+), calcd 301.9973. Anal. Calcd for $C_{13}H_{15}OSeCl$: C, 51.76; H, 5.01. Found: C, 51.70; H, 5.03.

The preparations of the 4-selenanols **1b,d,e**, **2b,d,e**, **3a**, and **4a** have been communicated.[7] Compounds **1a,c**, **2a,c**, **3b,c**, and **4b,c** were prepared from the corresponding 4-selenanones by reduction with lithium aluminum hydride in ether and aluminum isopropoxide in isopropyl alcohol. The procedure adopted to reduce the 4-selenanones and to separate the epimeric alcohols by column chromatography over neutral alumina was similar to the previously described method.[7] The yields, melting points, and solvents of crystallization of the 4-selenanols are recorded in Tables I and II.

Acetyl derivatives **1f,g**, **2f,g**, **3c**, and **4c** were prepared from the respective 4-selenanols by adapting a general procedure already described[7] and were crystallized from suitable solvents. Other relevant data are given in Table II.

Kinetics. The procedure employed was that published with subsequent modifications[2,3] and was carried out at 40 ± 0.1 °C in pyridine. In the case of 4-selenanols **1b,c** and **2b,c**, a mixture of carbon tetrachloride and *n*-butyl alcohol was used during titration to dissolve the acetate formed.

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Registry No. **1a**, 77340-61-5; **1b**, 74985-55-0; **1b** acetate, 74985-58-3; **1c**, 77270-25-8; **1d**, 74985-56-1; **1d** acetate, 74985-59-4; **1e**, 74985-57-2; **1e** acetate, 77270-26-9; **1f**, 77270-27-0; **1g**, 77270-28-1; **2a**, 77340-62-6; **2b**, 74966-36-2; **2b** acetate, 74966-40-8; **2c**, 77340-63-7; **2d**, 74966-37-3; **2d** acetate, 74966-41-9; **2e**, 74966-38-4; **2e** acetate, 77340-64-8; **2f**, 77340-65-9; **2g**, 77340-66-0; **3a**, 74966-43-1; **3a** acetate, 77270-29-2; **3b**, 77270-30-5; **3c**, 77270-31-6; **4a**, 74966-39-5; **4a** acetate, 77270-32-7; **4b**, 77270-33-8; **4c**, 77270-34-9; **5a**, 54232-38-1; **5b**, 54232-40-5; **5c**, 77270-35-0; 4-methyl-3-penten-2-one, 141-79-7; *p*-chlorobenzaldehyde, 104-88-1; 1-(*p*-chlorophenyl)-5-methyl-1,4-hexadien-3-one, 77270-36-1.