Ethyl Mesitonate Ethylene Ketal.—A solution of ethyl mesitonate in dry benzene (5.0 g, 0.03 mole in 25 ml) was refluxed with ethylene glycol (2 g, 0.03 mole) and p-toluenesulfonic acid (100 mg) for 12 hr. Water was removed in a Dean–Stark trap. The solution was washed with $NaHCO_3$ and dried over Na_2SO_4; the solvent was removed. The residue was distilled through a 10-cm Vigreux column to give 6 g of the ethylene ketal: yield 95%; bp 91–92° (7 mm). It exhibits ν_{max} (cm^{-1}) 1730 s, 1375 s, 1160 s; τ_{max} at 8.90 (singlet, 6 H), 8.82, (triplet, $J = 6$ cps, 6 H), 8.05 (singlet, 2 H), 6.15 (singlet, 4 H), 3.95 (quartet, $J = 6$ cps, 2 H). Anal. Calcd for $C_{11}H_{20}O_4$: C, 61.09; H, 9.32. Found: C, 60.89; H, 9.80.

4,4,5-Trimethyl-5-hydroxy-2-hexanone Ethylene Ketal.—A solution of the ester in ether (5 g, 0.023 mole in 20 ml) was gradually added to an ether solution of methyl lithium prepared by reacting lithium (0.84 g, 0.12 mole) with methyl iodide (8.5 g, 0.06 mole) in dry ether (65 ml). The reaction mixture was stirred at 10° overnight. It was decomposed with a saturated aqueous solution of NH_4Cl and dried over Na_2SO_4, the solvent evaporated, and the residue distilled under reduced pressure to give the alcohol (4.45 g): bp 60–61° (0.05 mm); yield 95%. It exhibits ν_{max} (cm^{-1}) 3500 w, 1375 s, 1150 s, 1040 s; τ_{max} at 9.00 (singlet, 6 H), 8.92 (singlet, 6 H), 8.70 (singlet, 3 H), 9.25 (singlet, 2 H), 6.60 (singlet, 1 H), 6.15 (singlet, 4 H). Anal. Calcd for $C_{11}H_{22}O_3$: C, 65.31; H, 10.96. Found: C, 65.01; H, 10.56.

2,4,4,5,5-Pentamethyltetrahydro-2-furanol.—A solution of the ketal alcohol in pentane (2.9 g, 0.014 mole in 30 ml) was vigorously stirred with HCl (20 ml, 0.5 N) for 5 hr in an ice water bath. The pentane layer was separated, washed three times with a dilute aqueous solution of $NaHCO_3$, and dried over Na_2SO_4. After removal of the solvent, the colorless oil was distilled under reduced pressure to give the furanol product (2.3 g) yield 83%, bp 28–30° (0.05 mm). A redistilled or sublimed sample solidified at 5° (mp 23°). Attempts to recrystallize the compound failed with petroleum ether, pentane, carbon tetrachloride, or alcohol. In preparations of the solid derivatives with benzoyl chloride, 3,5-dinitrobenzoyl chloride reagents were equally unsuccessful. The infrared and nmr of the compound were identical with those obtained from the photoproduct. The mass spectrum showed the P − 18 peak at m/e 140; the true parent peak at 158 was not found. Anal. Calcd for $C_9H_{18}O_2$: C, 68.31; H, 11.47. Found: C, 68.14; H, 11.26.

2,4,4,5,5-Pentamethyl-4,5-dihydrofuran.—The furanol (1.3 g) was heated under atmospheric pressure with an oil bath. Decomposition started at 125°; vigorous reaction occurred at 140–

160°. The dehydrated product (0.5 g) was obtained with some water: yield 45%; bp 123°; n^{24}D 1.4357. It showed identical infrared and nmr spectra with those of the photoproduct.

Ethyl Levulinate Ethylene Ketal.—Ethyl levulinate in benzene (100 g, 0.70 mole in 250 ml) was treated with ethylene glycol (43 g) using p-toluenesulfonic acid (150 mg) as catalyst. Water was removed in a Dean–Stark trap. Suitable work-up afforded a quantitative yield of the ketal ester (130 g), bp 110° (0.25 mm). It exhibits ν_{max} (cm^{-1}) 1745 s, 1150 s; τ_{max} at 8.98 (triplet, $J = 7$ cps, 3 H), 8.94 (singlet, 3 H), multiplet from 7.75–8.45, 4 H), 4.30 (singlet, 4 H), 4.15 (quartet, $J = 7$ cps, 2 H). Anal. Calcd for $C_9H_{16}O_4$: C, 57.43; H, 8.57; Found: C, 57.27; H, 8.78.

Methylation.—Ethyl levulinate ethylene ketal (28 g, 0.14 mole) was added to a solution of sodamide (0.30 mole) in liquid ammonia prepared according to the procedure of Khan[16] and co-workers (7 g of sodium, 0.14 mole and 0.2 g of ferric nitrate in 600 ml of liquid ammonia). After stirring for 2 hr, methyl iodide (60 g, 0.42 mole) was gradually added. The reaction mixture was vigorously stirred for 5 hr in a Dry Ice–acetone bath and was left overnight. It was decomposed with water (50 ml), extracted with ether, and dried over Na_2SO_4. After removal of the solvent by a water aspirator, the residue was distilled under reduced pressure to give 65% yield of a product (19 g), bp 60–64° (0.25 mm). The infrared and nmr spectra indicated that it was a mixture of largely monomethyl and a small amount of the dimethyl product. Consequently similar steps were taken to introduce a second methyl group (5 g of sodium, 40 g of methyl iodide, and 700 ml of liquid ammonia). The reaction afforded 35% yield of a product with boiling point considerably lower, 54–56° (0.050 mm). On comparison with ethyl mesitonate ethylene ketal, the two compounds proved to be identical in all respects.

Registry No.—1, 141-79-7; 5, 108-10-1; 7, 13144-88-2; 7 2,4-dinitrophenylhydrazone, 13144-89-3; 9, 13144-90-6; 10, 13144-91-7; 2-propanol, 67-63-0; ethyl mesitonate ethylene ketal, 13144-92-8; 4,4,5-trimethyl-5-hydroxy-2-hexanone ethylene ketal, 13144-93-9; ethyl levulinate ethylene ketal, 941-43-5; 9-phenylurethan, 13144-87-1.

(16) N. A. Khan, et al., "Organic Syntheses," Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1963, p 970.

# Stereoisomeric Thioxanthen-9-ol 10-Oxides

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The X-ray analysis of β-thioxanthen-9-ol 10-oxide (mp 206°) has revealed this to have the *trans* configuration. In the solid state the sulfur–oxygen bond occupies a pseudo-equatorial position while the HOCH dihedral angle is 34°. Configurations have also been assigned to the stereoisomeric 2-chlorothioxanthen-9-ol 10-oxides. Stereoselective oxidations of thioxanthen-9-ol and 2-chlorothioxanthen-9-ol are described.

Heterocyclic analogs of 9,10-dihydroanthracene (1a) possessing heteroatoms at either one or both of the *meso* positions (C-9 and C-10 in dihydroanthracene) generally exist in a conformation that is folded about an axis connecting the *meso* positions.[4] For atoms (M and/or M') which are configurationally stable under the conditions of investigation (e.g., the sulfoxide-
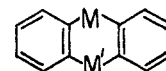
1a, M = CH$_2$; M' = CH$_2$
b, M = S(O); M' = S(O)
c, M = CHR; M' = CHR

sulfur atom at room temperature), appropriately substituted compounds may exhibit both configurational and conformational isomerism. These phenomena have been discussed for a number of molecular systems including 9,10-dihydroanthracenes (1a),[5a] thianthrene

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(2) Recipient of a National Science Foundation Teaching Assistant Summer Fellowship, 1965.

(3) The X-ray crystallographic study was performed in the Crystallography Laboratory of the University of Pittsburgh, Pittsburgh, Pa.

(4) E. E. Turner in "Chemistry of Carbon Compounds," Vol. I, E. H. Rodd, Ed., Elsevier Publishing Co., New York, N. Y., 1951, Chapter 9.

(5) (a) A. H. Beckett and B. A. Mulley, Chem. Ind. (London), 146 (1955); (b) S. Hosoya and R. G. Wood, ibid., 1042 (1957); (c) W. Michaels, O. Schindler, and R. Signer, Helv. Chim. Acta, 49, 42 (1966).
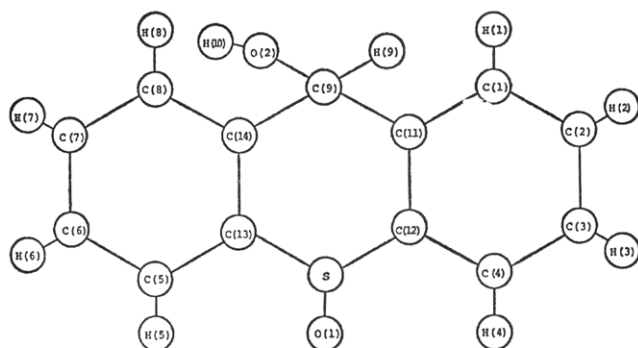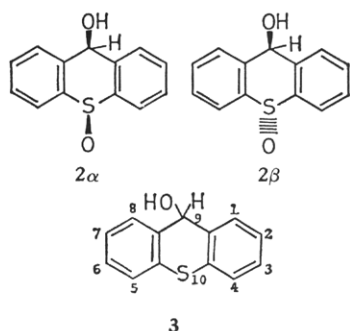
Figure 1.—The numbering system for *trans*-thioxanthen-9-ol 10-oxide (X-ray).

O = H
● = C
◉ = O
◎ = S

Figure 2.—*trans*-Thioxanthen-9-ol 10-oxide.

5,10-dioxides (**1b**),[5b] and thioxanthene 10-oxides (**1c**).[5c] Lansbury has recently discussed the stereochemical consequences of conformational mobility in the 7,12-dihydropleiadene system.[6] Detailed structural information (X-ray) is available for the 9,10-dihydroanthracene system[7] and for various oxides of thianthrene;[8] however, no such data are available for any thioxanthene 10-oxide (**1c**).

The thioxanthene ring system is particularly interesting since it may be viewed as a conformationally restricted diaryl sulfur compound. Furthermore, its two conformations represent, to the first approximation, the extremes of overlap between the sulfur n electrons and the aryl π system. Accordingly, we have begun an investigation into the stereochemistry of this system with the intent of evaluating the effects of conformation and configuration upon spectral properties and chemical reactivity. It would seem essential to establish an unequivocal assignment of configuration to a pair of stereoisomeric 9-substituted thioxanthene 10-oxides at the outset. Spectroscopic techniques have been applied to identify various stereoisomeric aryl-substituted thianthrene disulfoxides.[9] However, it may not be correct to apply, *a priori*, these same criteria to the assignment of configuration of stereoisomeric 9-substituted thioxanthene sulfoxides.[5c] The stereoisomeric thioxanthen-9-ol 10-oxides (**2α** and **2β**) have been chosen for unequivocal

2α   2β

3

assignment of configuration. These isomers possess substituents of comparable size at the *meso* positions

and, furthermore, provide an excellent framework for examining hydrogen bonding to diaryl sulfoxides.

Results and Discussion

Synthesis.—One may conceive of several alternative routes to these stereoisomeric 9-substituted thioxanthene sulfoxides. That route which involves the oxidation of the appropriate sulfide, thioxanthen-9-ol (**3**), is of interest since this molecular system may be useful in evaluating the effect of hydrogen bonding upon the stereoselectivity of the sulfide to sulfoxide conversion. Johnson and McCants[10] have noted that the steric course of oxidation at the sulfur atom of 4-substituted thianes may be determined by (a) thermodynamic control, (b) steric approach control, and (c) product development control. These workers have suggested that the oxidation of 4-substituted thianes to the corresponding sulfoxides involves *steric approach control* when the oxidants are peroxy reagents. Thus, the oxidation of 4-*t*-butylthiane with either *m*-chloroperbenzoic acid (in methylene chloride, 0°) or with hydrogen peroxide (in acetone, 25°) afforded a mixture composed of *ca.* 35% *cis*-sulfoxide and 65% *trans*-sulfoxide. Moreover, the stereoselectivity appears to be essentially independent of solvent. The oxidation of 4-*t*-butylthiane to the isomeric sulfoxides resulted in a distribution of isomers that was approximately constant for the following oxidant–solvent pairs: hydrogen peroxide in acetic acid, hydrogen peroxide in acetone, *t*-butyl hydroperoxide in benzene, *t*-butyl hydroperoxide in methanol, and *m*-chloroperbenzoic acid in methylene chloride.

It is interesting to compare these results with those obtained for the oxidation of thioxanthen-9-ol (**3**). The use of *m*-chloroperbenzoic in acetone afforded a mixture that contained substantial quantities of both stereoisomers (see Experimental Section). However, the use of aqueous hydrogen peroxide in acetone afforded only the *cis* isomer (**2α**). In addition to this dependence of isomer distribution upon the particular "peroxy" oxidant that is employed (for a given solvent),[11] we have observed a distinct dependence of stereoselectivity upon the solvent. *m*-Chloroperben-

(6) P. T. Lansbury, J. F. Bieron, and M. Klein, *J. Am. Chem. Soc.*, **88**, 1477 (1965).

(7) W. G. Ferrier and J. Iball, *Chem. Ind.* (London), 1296 (1954).

(8) S. Hosoya, *Acta Cryst.*, **21**, 21 (1966), and earlier papers in this series.

(9) K. Mislow, P. Schneider, and A. L. Ternay, Jr., *J. Am. Chem. Soc.*, **86**, 2957 (1964); T. Cairns, G. Eglinton, and D. T. Gibson, *Spectrochim. Acta*, **20**, 159 (1964).
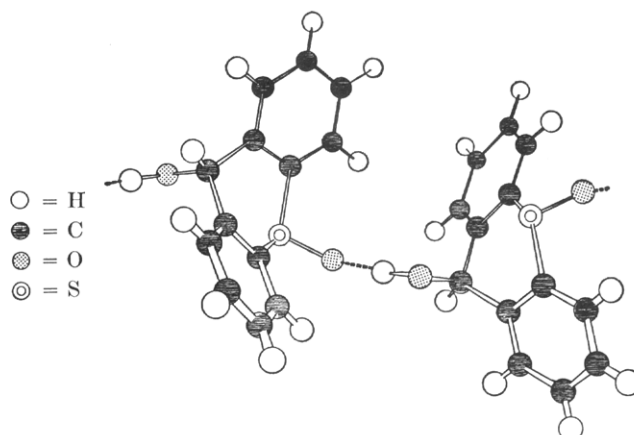
(10) C. R. Johnson and D. McCants, Jr., *J. Am. Chem. Soc.*, **87**, 1109 (1965).

(11) It should be noted that the solvent is not purely acetone, but rather an acetone–water mixture, when 30% hydrogen peroxide is the oxidant.

Table I

Some Planes of Atoms

Coefficients in $AX + BY + CZ - D = 0$ referred to the crystallographic axes
(coordinates in angstrom units)

Plane no.	Atoms forming plane	A	B	C	D
1	C(11)–C(12)–C(13)–C(14)	−0.3719	−0.7349	0.6730	−4.6408
2	C(5)–C(6)–C(7)–C(8)–C(13)–C(14)	0.5541	0.8116	−0.4111	5.1424
3	C(1)–C(2)–C(3)–C(4)–C(11)–C(12)	−0.1074	−0.5721	0.7767	−2.4146
4	SO(1)–O(2)–C(9)	0.5677	0.3152	0.4310	3.5549
5	C(9)–O(2)–H(10)	0.8930	−0.1284	−0.0080	3.6004
6	C(9)–O(2)–H(9)	0.6088	0.2823	0.3957	3.6341

zoic acid was used to oxidize 2-chlorothioxanthen-9-ol (4) to the corresponding isomeric sulfoxides. When acetone was the solvent, the *trans* isomer (5β) was produced in large excess while when methylene chloride was the solvent the other stereoisomer (5α) was produced in excess (see Experimental Section).

Thus, it seems clear that the 4-substituted thiane system[10] does not serve as a model for the sulfide to sulfoxide conversion in this series. This deviation from a behavior that may be considered to be controlled by steric factors probably reflects the influence of hydrogen bonding and/or stereoelectronic factors upon the oxidation of conjugated sulfides. A detailed analysis of these and related data will be the subject of a future communication.

X-Ray Analysis.—The X-ray analysis proves that β-thioxanthenol sulfoxide is the *trans* isomer. The numbering of the molecule *for the purposes of this discussion* is presented in Figure 1, while the actual structure is illustrated in Figure 2. The molecule is best described in terms of the planes of atoms that are given in Table I.

The dihedral angle between the planes of the benzene rings is 132.4°. The sulfur atom is displaced 0.04 A below the plane of C(5)–C(8)–C(14)–C(13)–C(6)–C(7), but is 0.06 A above the plane of the other benzene ring whereas C(9) is 0.05 A above and 0.006 A below the respective planes. The plane containing atoms C(12)–C(11)–C(13)–C(14) is almost perpendicular to the plane formed by S–C(9)–O(1)–O(2); the dihedral angle made by these two planes is 90.7°. O(1) lies 0.06 A below the C(12)–C(11)–C(14)–C(13) plane, but S, C(9), and O(2) are 0.66, 0.51, and 1.93 A, respectively, above the plane, which demonstrates clearly the *trans* configuration of the oxygen atoms. The difference between the distance of atoms C(9) and O(2) from this plane equals the C(9)–O(2) bond length. Another dihedral angle of interest is the one between the C(9)–O(2)–H(9) and C(9)–O(2)–H(10) planes which is 34°, showing that H(10) and H(9) are in a skew conformation intermediate to the *cis* and *gauche* forms with respect to the C(9)–O(2) bond.

The bond lengths and valency angles are listed in Tables II and III. If the S=O bond length is adjusted to compensate for the effect of thermal motion by assuming a riding motion for the oxygen atom,[12] the distance becomes 1.50 A. This corresponds to bond number 1.9, according to simple valence bond theory.[13] After the thermal correction is made, the C–S bonds average 1.78 A. This corresponds to a bond number 1.08. The other bond distances and angles are the ex-

Table II

Bond Lengths and Their Estimated Standard Deviations[a]

Bond	Length, A	Estd std dev, A
C(11)–C(1)	1.39	0.015
C(1)–C(2)	1.39	0.015
C(2)–C(3)	1.37	0.020
C(3)–C(4)	1.41	0.018
C(4)–C(12)	1.35	0.014
C(12)–S	1.80	0.012
S–C(13)	1.75	0.012
C(13)–C(5)	1.38	0.013
C(5)–C(6)	1.38	0.019
C(6)–C(7)	1.39	0.021
C(7)–C(8)	1.39	0.016
C(8)–C(14)	1.37	0.015
C(14)–C(9)	1.51	0.014
C(9)–C(11)	1.50	0.014
C(11)–C(12)	1.38	0.016
C(13)–C(14)	1.40	0.016
C(9)–O(2)	1.42	0.015
S–O(1)	1.484	0.008
O(2)–H(10)	1.08	0.15
O(1)···O(2)	2.75	0.012
O(1)···H(10)	1.68	0.15

[a] The last three entries in the table refer to distances between atoms involved in a hydrogen bond.

pected ones, within the experimental error of the analysis.

The molecular packing scheme is a simple one indeed. Molecules related by a twofold screw axis are hydrogen bonded through atoms O(1)···H(10)–O(2) into an infinite chain. All of the other intermolecular distances correspond to normal van der Waals contacts.

Absorption Spectra.—The stereoisomeric thioxanthen-9-ol 10-oxides (2α, 2β) possess different absorption spectra in the infrared region. Thus, the *cis* isomer (2α) exhibits (see Experimental Section) two strong bands in the region from 1100 to 1000 cm⁻¹ while the *trans* isomer (2β) exhibits three strong bands in the same region. Furthermore, 2α possesses one of these bands between 1050 and 1000 cm⁻¹ while 2β possesses two bands in this region. While other differences exist between the solid-state (Nujol mull) spectra of 2α and 2β, *this* variation is most striking. This, however, is not surprising since both the S–O and the C–O stretching modes are expected to be located in this region.[9,14]

Spectral differences between 2α and 2β are not limited to the infrared region. The ultraviolet spectra of these diastereomers also are markedly different. Both isomers possess an intense short-wavelength transition; however, this absorption occurs at a longer wavelength for 2β than for 2α (214 vs. 204 mμ). More-

(12) W. R. Busing and H. A. Levy, *Acta Cryst.*, **18**, 142 (1964).
(13) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, pp 320–323.
(14) H. H. Zeiss and M. Tsutsui, *J. Am. Chem. Soc.*, **75**, 897 (1953).

TABLE III

VALENCY ANGLES AND THEIR ESTIMATED STANDARD DEVIATIONS

Atoms	Angle, deg	Estd std dev, deg
O(1)–S–C(12)	107.1	0.8
O(1)–S–C(13)	107.8	0.8
C(12)–S–C(13)	97.5	0.7
O(2)–C(9)–C(11)	108	1.1
O(2)–C(9)–C(14)	110	1.1
C(11)–C(9)–C(14)	112	1.1
S–C(12)–C(11)	119	1.1
S–C(12)–C(4)	117	1.4
C(4)–C(12)–C(11)	123	1.4
C(12)–C(11)–C(1)	117	1.4
C(12)–C(11)–C(9)	120	1.3
C(1)–C(11)–C(9)	122	1.3
S–C(13)–C(14)	120	1.0
S–C(13)–C(5)	119	1.0
C(5)–C(13)–C(14)	121	1.2
C(13)–C(14)–C(8)	120	1.2
C(13)–C(14)–C(9)	120	1.1
C(8)–C(14)–C(9)	120	1.2
C(12)–C(4)–C(3)	119	1.6
C(4)–C(3)–C(2)	119	1.7
C(3)–C(2)–C(1)	120	1.7
C(2)–C(1)–C(11)	121	1.5
C(13)–C(5)–C(6)	119	1.3
C(5)–C(6)–C(7)	120	1.5
C(6)–C(7)–C(8)	121	1.5
C(7)–C(8)–C(14)	119	1.3
C(9)–O(2)–H(10)	102	6
O(2)–H(10)–O(1)[a]	172	6

[a] Refers to the angle between atoms involved in an intermolecular hydrogen bond.

over, absorption in the 260-mμ region is more intense for 2β than for 2α. The critical features of the ultraviolet spectra are presented in Table IV.

TABLE IV

ULTRAVIOLET SPECTRA

Compound	Absorption characteristics[a–c]
2α	272 (866); 232 (8300); *204* (41,900)
2β	285 (558); 273 (1620); *250* (4420); 233 (8060); *214* (42,000)
5α	253 (6350); 234 (12,900); *205* (44,300)
5β	283 (1100); *255* (6690); 235 (11,000); *215* (39,000)

[a] Spectra in 95% ethanol. [b] Wavelengths are in millimicrons, molecular extinction coefficients (ε) in parentheses; maxima are in italics; all other values refer to shoulders or inflections. [c] Several very broad, poorly defined shoulders in the longer wavelength region have been deleted; complete curves are available upon request.

It is now possible to unequivocally assign configurations to some other pairs of stereoisomeric 9-substituted thioxanthene sulfoxides. However, when spectral parameters are employed, such assignments would seem most credible when the spectra of these isomers differ from one another in the same manner as do the spectra of 2α and 2β. On this basis we have assigned the *trans* configuration to that isomer (5β) of 2-chlorothioxanthen-9-ol 10-oxide which melts at 194°.

To wit, 5α exhibits three major absorptions in the 1100–1000-cm⁻¹ region of the infrared while four bands are present in the spectrum of 5β. (The spectrum of 2α is simpler in this region than is the spectrum of 2β.)

Moreover, for 5α one of these bands is located in the 1050–1000-cm⁻¹ region while two bands occur in this range for 5β (see Experimental Section). (Isomers 2α and 2β show similar behavior.) The ultraviolet spectrum of 5α differs from that of 5β in the same manner as the spectrum of 2α differs from that of 2β (see Table IV).

Experimental Section[15]

X-Ray Analysis.—Single crystals of β-thioxanthen-9-ol 10-oxide suitable for an X-ray diffraction analysis were grown by slowly crystallizing the compound from hot ethyl acetate. They are lathlike in habit and possess monoclinic symmetry. From the systematic extinctions, $h0l$ absent when h is odd and $0k0$ absent when k is odd, the space group is determined uniquely to be $P2_1/a$. The unit cell dimensions were obtained from measurements made on equatorial Weissenberg photographs using Cu radiation. They are $a = 11.75$, $b = 12.40$, $c = 8.25$, all ±0.03 Å; $β = 116° 15' ± 10'$. The density measured by flotation in aqueous stannic chloride is 1.34 g cm⁻³, whereas the calculated density based upon the X-ray data is 1.42 g cm⁻³.

The multifilm equiinclination Weissenberg photographic technique was used, with Cu Kα radiation, for collecting the intensity data from single crystals mounted about the b and c axes, respectively. The intensities were estimated visually by comparison with a standard scale. The interfilm scaling, the Lorentz-polarization and spot-shape corrections, reduction to structure factor magnitudes, and the interlayer correlations were carried out on the IBM 1620 computer using a series of programs.[16] No extinction or absorption corrections were made. The structure factors were scaled by a Wilson plot and the signs of 479 normalized structure factors were uniquely determined by a direct method procedure programmed for the IBM 1620.[17] An E map synthesis[18] gave well-resolved peaks indicating the atomic positions within the unit cell for the molecule. Structure factors calculated with these coordinates and a single over-all temperature factor gave an R index ($\Sigma|F_o - F_c|/F_o$) equal to 0.433 for all of the 1145 observed reflections.

The parameters were refined on the IBM 7090 using a full-matrix least-squares procedure.[19,20a] $\Sigma w(F_o - KF_c)^2$ is the function minimized. The weighting scheme was that of Hughes with F_{min} equal to 2.[20b] Two isotropic followed by three anisotropic cycles were run. The R index after the isotropic cycles was 0.169 and after the final anisotropic cycle was 0.124. The positional parameters for the hydrogen atoms bonded to the aromatic rings were fixed in this calculation by assuming a C–H bond length of 1 Å in the direction opposite to that of the ring diagonal from the carbon atom to which it was bonded. The corresponding parameters for the hydrogen atom bonded to the bridge carbon atom were calculated similarly by assuming a 1-Å bond length but tetrahedral coordination for the carbon atom. The hydroxyl hydrogen coordinates were obtained from an $(F_o - F_c)$ difference synthesis. The hydrogen atoms were assigned the same temperature factors as the carbon atoms to which they are bonded. Unobserved reflections were omitted from calculations of the R index. The atomic coordinates, the

(15) Melting points were obtained in a Mel-Temp apparatus and are corrected. Infrared spectra were obtained as Nujol mulls and were recorded on a Beckman Model IR-8. Ultraviolet spectra were determined on a Cary Model 15. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn. Thin layer chromatographies were performed employing glass plates coated with silica containing a fluorescent indicator. Development was achieved with ethyl acetate, benzene, or chloroform. Both ultraviolet light and iodine vapor were used for visualization.

(16) Crystallographic Computing Programs for the IBM 1620 Computer, University of Pittsburgh Technical Report No. 43 and 45, 1963.

(17) P. T. Beurskens, Technical Report on Sign Correlation by the Sayre Equation, The Crystallography Laboratory, University of Pittsburgh, 1963.

(18) I. L. Karle, H. Hauptman, J. Karle, and A. B. Wing, *Acta Cryst.*, **11**, 257 (1958).

(19) W. R. Busing, K. O. Martin, and H. A. Levy, ORFLS A FORTRAN Crystallographic Least Squares Program, Oak Ridge National Laboratory, Report ORNL-TM-305.

(20) (a) The atomic form factors were taken from the "International Table for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962. The real and imaginary dispersion corrections used for sulfur are 0.3 and 0.6, respectively, independent of sin θ. (b) E. W. Hughes, *J. Am. Chem. Soc.*, **63**, 1737 (1941).

Table V

The Atomic Coordinates and Thermal Parameters and Their Estimated Standard Deviations[a]

Atom	Fractional coordinates × 10⁴			Thermal parameters[b] × 10⁵					
	X	Y	Z	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
S	2292 (2)	4027 (2)	1239 (3)	979 (21)	534 (17)	2088 (47)	0 (17)	940 (26)	7 (26)
C(1)	5802 (9)	3775 (8)	1538 (14)	911 (82)	666 (87)	2179 (196)	298 (73)	775 (110)	346 (117)
C(2)	6429 (11)	4636 (10)	2646 (15)	1010 (107)	851 (103)	2345 (229)	−179 (94)	560 (138)	368 (139)
C(3)	5791 (11)	5324 (11)	3257 (14)	1325 (130)	922 (107)	1800 (214)	−135 (101)	581 (146)	152 (134)
C(4)	4502 (10)	5123 (9)	2797 (13)	1342 (111)	691 (86)	1507 (164)	−178 (83)	818 (117)	1 (110)
C(5)	594 (10)	3965 (10)	−2294 (15)	841 (87)	780 (94)	2544 (240)	−171 (84)	493 (121)	163 (137)
C(6)	161 (11)	3625 (10)	−4055 (17)	1015 (109)	792 (93)	2763 (280)	−103 (90)	457 (157)	512 (148)
C(7)	936 (12)	2989 (10)	−4538 (16)	1490 (137)	767 (96)	2027 (222)	−42 (95)	381 (154)	24 (132)
C(8)	2109 (11)	2634 (9)	−3260 (13)	1365 (116)	410 (72)	1908 (176)	−48 (73)	714 (127)	61 (98)
C(9)	3831 (9)	2635 (8)	−87 (14)	1024 (92)	565 (77)	2365 (222)	337 (73)	788 (124)	153 (115)
C(11)	4538 (8)	3567 (8)	1091 (13)	836 (84)	472 (62)	1864 (181)	153 (67)	637 (109)	294 (102)
C(12)	3924 (9)	4277 (8)	1729 (12)	1061 (92)	534 (70)	1344 (162)	48 (66)	752 (109)	−37 (94)
C(13)	1765 (8)	3616 (7)	−1012 (12)	781 (77)	383 (59)	1712 (161)	−212 (60)	522 (95)	65 (92)
C(14)	2536 (10)	2973 (8)	−1506 (13)	1230 (110)	403 (65)	1861 (186)	−9 (71)	872 (124)	73 (100)
O(1)	1705 (6)	5088 (6)	1229 (10)	1081 (70)	656 (58)	3056 (187)	149 (55)	1235 (103)	−190 (85)
O(2)	3714 (7)	1820 (6)	1042 (10)	1450 (94)	627 (59)	2180 (159)	71 (58)	745 (108)	398 (82)
H(1)	6266	3276	1071						
H(2)	7329	4776	2983						
H(3)	6253	5958	4045						
H(4)	4031	5622	3277						
H(5)	48	4461	−1955						
H(6)	−693	3872	−4978						
H(7)	642	2751	−5800						
H(8)	2656	2130	−3617						
H(9)	4294	2343	−789						
H(10)	3600	1100	250						

[a] The estimated standard deviations are multiplied by the same factor as the corresponding coordinate or thermal parameter. [b] Coefficients in the form, $\exp[-(h^2 b_{11} \ldots \ldots 2kl b_{23})]$.

anisotropic temperature coefficients, and their standard deviations are listed in Table V. The observed and calculated structure factors are listed in Table VI.[21] The numbering of the atoms is shown in Figure 1.

Thioxanthen-9-ol (3).—Thioxanthen-9-one (6) (2.10 g, 9.9 mmoles) was reduced with an excess of sodium borohydride (0.5 g, 0.13 mole) in 95% ethanol (50 ml). After stirring for 45 min, 10 ml of water was added and the mixture warmed on a steam bath. Addition of ice caused the precipitation of 3 which was then washed with water and air dried. There resulted 2.0 g (9.3 mmoles, 94%) of 3, mp 102–105° (lit.[22] mp 104–105°). The infrared spectrum[23] possessed absorption at 1037, 1050, and 1092 cm⁻¹.

2-Chlorothioxanthen-9-ol (4).—2-Chlorothioxanthen-9-one (15.0 g, 0.061 mole) was reduced in the same manner as was 6. Thus, there was obtained 12.6 g (0.051 mole, 83%) of 2-chloro-thioxanthen-9-ol, mp 127–129° (lit.[24] mp 127–129°). The infrared spectrum[23] possessed absorption at 1047, 1059, and 1090 cm⁻¹.

α-Thioxanthen-9-ol 10-Oxide (2a).—Hydrogen peroxide (30%, 2.3 g, 0.02 mole) in acetone (40 ml) was added to a stirred solution of 3 (5.0 g, 0.023 mole) in acetone (70 ml) at 25°. After 12 hr the solution was treated with magnesium sulfate and a small amount (ca. 1 g) of sodium sulfite. The solids were removed by filtration and the resulting solution was concentrated via a stream of nitrogen to afford a yellow solid. Thin layer chromatography showed the presence of only two compounds—cis-thioxanthen-9-ol 10-oxide (ca. 80%) and thioxanthen-9-one (ca. 20%). This yellow solid was extracted with benzene and the residual white solid recrystallized from ethyl acetate to afford 1.7 g (7.4 mmoles,

32%) of 2α, mp 218–218.5°. The infrared spectrum[23] possessed absorptions at 1010 and 1098 cm⁻¹.

Anal. Calcd for $C_{13}H_{10}O_2S$: C, 67.80; H, 4.38; S, 13.93. Found: C, 68.00; H, 4.36; S, 13.84.

β-Thioxanthen-9-ol 10-Oxide (2β).—A solution of m-chloro-perbenzoic acid (4.66 g, 27 mmoles) in acetone (110 ml) was added to a stirred solution of 3 (6.0 g, 0.028 mole) in acetone (110 ml) at 0°. After stirring at 0° for 11 hr, the resultant mixture was filtered; the solution was washed with 100 ml of saturated sodium bicarbonate solution and then concentrated *in vacuo*. This suspension was extracted with five 50-ml portions of methylene chloride. The extracts were dried (magnesium sulfate) and concentrated (nitrogen stream) to afford a yellow solid. Thin layer chromatography showed this solid to be a mixture of 6, 2α, and 2β. The *trans* isomer (2β) constituted ca. 60% of the mixture of 2α and 2β while thioxanthone (6) comprised ca. 20% of the entire mixture.[25] This yellow solid was extracted with benzene and the residual white solid recrystallized with acetone and ethyl acetate to afford 1.2 g (5.2 mmoles, 19%) of 2β, mp 205–206°. The infrared spectrum is more complex than that of 2α and exhibited absorptions[23] at 1002, 1023, and 1077 cm⁻¹.

Anal. Calcd for $C_{13}H_{10}O_2S$: C, 67.80; H, 4.38; S, 13.93. Found: C, 67.57; H, 4.20; S, 13.88.

α-2-Chlorothioxanthen-9-ol 10-Oxide (5α).—m-Chloroper-benzoic acid (0.69 g, 4.0 mmoles) dissolved in methylene chloride (75 ml) was added to a stirred solution of 4 (1.0 g, 4.0 mmoles) in methylene chloride (50 ml) at 0°. After 12 hr at 0°, the resultant mixture was filtered and the filtrate washed (saturated sodium bicarbonate) and dried (magnesium sulfate). Concentration of the methylene chloride solution afforded a yellow solid. Thin layer chromatography of this solid showed the presence of three compounds: 2-chlorothioxanthen-9-one (ca. 15%), 5α (ca. 70%), and 5β (ca. 15%). Extraction of this solid with benzene followed by recrystallization (ethyl acetate) of the residue afforded 0.40 g (1.52 mmoles, 38%) of cis-2-chlorothioxanthen-9-ol 10-oxide, 5α, mp 220–222°. The infrared spectrum of 5α exhibited absorption at 1028 (s), 1066 (s), and 1100 cm⁻¹.[23]

Anal. Calcd for $C_{13}H_9ClO_2S$: C, 58.98; H, 3.43; S, 12.11; Cl, 13.39. Found: C, 58.76; H, 3.21; S, 11.94; Cl, 13.62.

(21) Table VI has been deposited as Document No. 9388 with the American Documentation Institute Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and remitting $1.25 for photoprints or $1.25 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to Chief, Photoduplication Service, Library of Congress.

(22) H. F. Oehlschlaeger and I. R. MacGregor, *J. Am. Chem. Soc.*, **72**, 5332 (1950).

(23) Only those bands of moderate to strong intensity that occur in the 1000–1100-cm⁻¹ region are listed.

(24) C. Pfizer and Co., British Patent 863,699 (1961).

(25) The relative amounts of 2α and 2β were determined by preparative thin layer chromatography.

β-2-Chlorothioxanthen-9-ol 10-Oxide (5β).—*m*-Chloroperbenzoic acid (0.69 g, 4.0 mmoles) dissolved in acetone (75 ml) was added to a stirred solution of 4 (1.0 g, 4.0 mmoles) in acetone (50 ml) at 0°. After 11 hr at 0° the reaction mixture was worked up as described for 2β to afford 0.5 g (1.89 mmoles, 47%) of 5β, mp 192–194°. Thin layer chromatography of the initially isolated reaction product showed the presence of three compounds: 2 chlorothioxanthone (*ca.* 15%), 5α (*ca.* 5%), and 5β (*ca.* 80%).[26] The infrared spectrum of 5β exhibited absorption at 1010, 1031, 1071, and 1100 cm^{-1}.[23]

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(26) The different stereoselectivities noted in the synthesis of **2β** and **5β** appear to reflect a dependence upon concentration and not simply upon differences between **3** and **4**.

Group VIII Metal Catalyzed Reactions of Organosilicon Hydrides with Amines, Hydrogen Halides, and Hydrogen Sulfide

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The stereochemistry and synthetic utility of the group VIII noble metal catalyzed reactions of silicon–hydrogen bonds with nonhydroxyllic compounds containing active hydrogen have been studied. The reaction provides a quick, convenient method for preparation of silylamines, silanethiols, and halosilanes. Various catalysts have been evaluated from both a preparative and a stereochemical viewpoint.

The group VIII metal catalyzed reaction of silanes containing a silicon–hydrogen bond with a hydroxyl group has been extensively studied.[1] However, there are very few reported reactions[2,3] between the silicon–hydrogen linkage and other compounds containing active hydrogen. We therefore undertook a study of the utility of this reaction for placing various non-oxygenated groups on silicon (eq 1), while simultaneously investigating the stereochemistry of the transformation.

$$R_3SiH + HX \cdots \xrightarrow{\text{catalyst}} R_3SiX \cdots + H_2 \qquad (1)$$

Since optically active α-naphthylphenylmethylsilane (R$_3$Si*H) is readily available,[4] it was used to study both the synthetic utility and the stereochemistry of the reaction (Table I). The most striking result in Table I is that many of the reactions proceed with *inversion*. This result has also been found for oxygen functions.[1] This stereochemical result would seem to rule out the operation of a four-center mechanism such as 1 in these cases.

1
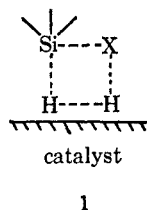
There are other interesting stereochemical points in Table I. An alumina support always gave better stereochemical results (reactions 1, 4, 12, 15, and 18) than a carbon support (2, 3, 10, 14, and 16), which

gave racemic product in the aminosilane cases. This was not caused by the extra 5% palladium on the surface since 5% Pd–C also gave racemic product in reaction 5. Conversely, the carbon-supported catalyst appeared to be more active in the amine reactions.

The retention stereochemistry observed for HCl and H$_2$S is hard to rationalize. For instance, acid strength does not give a correlation, since hydrogen fluoride, which reacts with inversion, is intermediate between the two in acidity. The only similarity between both reagents seems to be that chlorine and sulfur are both second-row elements, but this may merely be a coincidence. More information concerning what takes place on catalyst surfaces is necessary before the mechanism of this reaction can be known with any degree of certainty.

To our knowledge, metal-catalyzed reactions of hydrogen halides or sulfur compounds with silicon–hydrogen bonds had not been reported previously and it was of interest to study this reaction in some detail. In Table II are found the results of reactions with triethylsilane. These results clearly show that this is a good method for preparation of halosilanes from compounds having a silicon–hydrogen bond. For chloro- and bromosilanes this may not offer much of an advantage over the reaction using the elemental halogen.[5,6] However, if there are organic groups present which can be halogenated by chlorine[6] but not by hydrogen chloride, the catalytic method may be advantageous.

In the case of fluorosilanes, the situation is different—direct halogenation is impossible.[5] The usual methods[7] involve replacement of chloride by fluoride using reagents such as ammonium fluoride and zinc fluoride or

(1) L. H. Sommer and J. Lyons, *J. Am. Chem. Soc.*, **89**, 1521 (1967).
(2) L. Birkofer, E. Bierwirth, and A. Ritter, *Chem. Ber.*, **94**, 821 (1961).
(3) J. C. Saam and J. L. Speier, *J. Org. Chem.*, **24**, 119 (1959).
(4) L. H. Sommer, C. L. Frye, G. A. Parker, and K. W. Michael, *J. Am. Chem. Soc.*, **86**, 3271 (1964).

(5) V. Bazant, V. Chvalovsky, and J. Rathousky, "Organosilicon Compounds," Vol. I, Academic Press Inc., New York, N. Y., 1965, p 29.
(6) C. Eaborn, "Organosilicon Compounds," Butterworth London, 1960, pp 168–169, 209–210.
(7) Reference 6, pp 174–176.