Anal. Calcd for $C_{21}H_{21}NS_2$: C, 71.8; H, 6.0; N, 4.0; S, 18.2. Found: C, 71.8; H, 5.8; N, 3.9; S, 18.2.

Cyclohexylamine gave XIIc, orange, mp 160–161° (methylcyclohexane).

Anal. Calcd for $C_{23}H_{23}NS_2$: C, 73.2; H, 6.1; N, 3.7; S, 17.0. Found: C, 73.1; H, 5.9; N, 3.6; S, 16.9.

Methylation of Xa to XIII.—Methyl iodide (5 ml) was added through the condenser to a stirred refluxing mixture of 1.35 g (3.64 mmol) of Xa in 20 ml of nitromethane. After 1 hr, the solution was cooled, diluted with a little ether, and filtered, yielding 1.85 g (99%) of orange product. In an ordinary capillary melting point determination, it lost methyl iodide around 160° and then gave the melting point (199–200°) of Xa. A melting point of 166° could be observed by insertion into the bath at 160°, but this seems less reproducible. Crystallization occurred readily from ethanol or methanol. Aniline or methylaniline in refluxing acetic acid reversed the methylation reaction, regenerating Xa.

Anal. Calcd for $C_{24}H_{20}INS_2$: C, 56.1; H, 3.9; I, 24.8; N, 2.7; S, 12.5. Found: C, 56.3; H, 3.7; I, 24.7; N, 2.9; S, 12.4.

This combined rapidly with 1 mol of iodine in methanol solution to give the *triiodide* (XIIIa), mp 150–150.5°, which separated as golden crystals from *n*-propyl alcohol.

Anal. Calcd for $C_{24}H_{20}I_3NS_2$: C, 37.6; H, 2.6; I, 49.7; N, 1.8. Found: C, 37.8; H, 2.6; I, 49.6; N, 1.8.

3-(2-N-Methylanilino-1-phenylvinyl)-5-phenyl-1,2-dithiolium Iodide (VII).—A mixture of 2.27 g (5.0 mmol) of 3-(2-methylthio-1-phenylvinyl)-5-phenyl-1,2-dithiolium iodide (V) and 0.65 ml (0.64 g, 6.0 mmol) of N-methylaniline in 50 ml of methanol was stirred at reflux for 5 hr, cooled, diluted with ether, and chilled to −78°, yielding 1.24 g (49%) of greenish product, mp 185–187°. *n*-Propyl alcohol gave dark brown crystals, mp 196.5–197°, showing marked melting-point depression on admixture with XIII.

Anal. Calcd for $C_{24}H_{20}INS_2$: C, 56.1; H, 3.9; I, 24.8; N, 2.7; S, 12.5. Found: C, 56.1; H, 3.8; I, 24.4; N, 2.7; S, 12.4.

When the reaction was continued somewhat longer, the product was obtained in lower yield together with VIII, which separated on cooling before dilution with ether.

The corresponding triiodide VIIa gave bronze crystals, mp 149–150° dec, from *n*-propyl alcohol, showing a marked melting point depression on admixture with XIIIa.

Anal. Calcd for $C_{24}H_{20}I_3NS_2$: C, 37.6; H, 2.6; I, 49.7; N, 1.8; S, 8.3. Found: C, 37.6; H, 2.6; I, 50.1; N, 1.7; S, 8.5

At a concentration of 10 mg/l. in ethanol containing a little Cellosolve, VII showed an absorption band at λ_{max} 480 (ϵ 16,100) (Figure 3). Absorption in the same region is reported in a recent brief communication on salts of similar type.[11]

Registry No.—I, 3354-37-8; II, 16717-54-7; III, 16717-55-8; V, 16717-56-9; VI, 16717-57-0; VII, 16717-58-1; VIIa, 16717-59-2; IX, 16717-60-5; Xa, 16753-66-5; Xb, 16753-67-6; Xc, 16753-68-7; Xd, 16753-69-8; Xe, 16753-70-1; XIa, 16753-71-2; XIIa, 16753-72-3; XIIb, 16753-73-4; XIIc, 16753-74-5; XIII, 16717-61-6; XIIIa, 16717-62-7; XIV, 16717-63-8.

Acknowledgment.—The author is greatly indebted to Mrs. Maryellen Kish for technical assistance, to J. J. Kobliska and his staff for microanalyses, and to Miss Vera Jordan for absorption spectra.

[11] R. Meyer and H. Hartmann, *Z. Chem.*, **6**, 312 (1966).

Preparation of Silylalkanethiols

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Silylalkyl ethanethiolates with chloro, acetoxy, hydroxy, and alkoxy substituents attached to silicon were prepared by the reaction of ethanethiolic acid with corresponding alkenylsilanes. The effects of the substituents on silicon on the reactivity of vinylsilanes toward thiols or ethanethiolic acid were found to be additive. Ethanethiolic acid reacts with most vinylsilanes to give two adducts, $\equiv SiCH_2CH_2SAc$ (major) and $\equiv SiCHCH_3SAc$ (minor). Silylalkanethiols were prepared by methanolysis or ammonolysis of some of these esters. Several new types of silylalkanethiols prepared in this manner are $HN(SiMe_2CH_2CH_2SH)_2$ and $Me_2XSiCH_2CH_2SH$ where X is Cl-, MeO-, HO-, and AcO-. The log of the relative rate constants (the rate constant for hexene-1 ÷ 1) for addition of thiols and also of silicon hydrides was found to show a linear correlation with the sum of substituent constants C for the groups R, R′, and R″ in compounds of the formula $RR'R''SiCH{=}CH^2$.

Ethanethiolic acid adds to the double bond of olefins by a free-radical process with great efficiency. Olefins substituted in nearly all possible ways form corresponding alkyl ethanethiolates in good yields. A few examples of silicon-containing olefins of the types $R_3SiC_nH_{2n-1}$ and $O(SiR_2C_nH_{2n-1})_2$ have been used in which R was either an alkyl or phenyl group.[1-6]

We have found that alkenylsilanes with chloro, alkoxy, and acetoxy substituents on silicon can be converted into corresponding silylalkyl ethanethiolates in excellent yield. We observed no interference from any of these substituents. Aminosilylalkyl ethanethiolates could not be prepared in the same manner, however, because ethanethiolic acid reacts rapidly with amino groups on silicon to form thionoacetoxysilanes.[7]

Ethanethiolic acid reacts with vinylsilanes to form two isomeric adducts (eq 1). Only terminal adducts to

$$\equiv SiCH{=}CH_2 + AcSH \longrightarrow \underset{\text{major}}{\equiv SiCH_2CH_2SAc} + \underset{\text{minor}}{\equiv SiCH(CH_3)SAc} \quad (1)$$

vinylsilanes had been reported by workers previous to Wetterlin[8] who was the first to report that two adducts analogous to the above form during the reaction of vinylsilanes with some thiols.

Silylalkyl ethanethiolates were converted into silylalkanethiols by methanolysis or ammonolysis. Methanolyses were run in an excess of methanol containing

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[1] P. V. Bonsignore, C. S. Marvel, and S. Bonerjee, *J. Org. Chem.*, **25**, 235 (1960).

[2] P. W. Gawrys and H. W. Post, *ibid.*, **27**, 634 (1962).

[3] W. Stamm, *ibid.*, **28**, 3264 (1963).

[4] C. S. Marvel and H. N. Cripps, *J. Polym. Sci.*, **9**, 53 (1953).

[5] V. F. Mironov and N. A. Pogonkina, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, **85**, (1959).

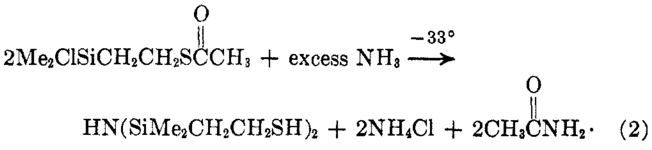
[6] A. D. Petrov, V. F. Mironov, and V. G. Glukhontsev, *J. Gen. Chem. USSR*, **27**, 1535 (1957).

[7] G. A. Gornowicz and J. W. Ryan, *J. Org. Chem.*, **31**, 3439 (1966).

[8] K. Wetterlin, *Acta Chem. Scand.*, **18**, 899 (1964).

a catalytic amount of sodium methoxide. Bases were found to be more effective than acids as catalysts. A large excess of methanol was needed to prevent the formation of considerable amounts of by-products. These appeared to be condensation products of the esters.

A variety of silylalkanethiols and related compounds can be prepared by ammonolysis of silylalkyl ethanethiolates. Ammonolysis of 2-dimethylchlorosilylethyl ethanethiolate gave a somewhat indefinite product (I) believed to have formed by loss of NH_3 from *sym*-bis(2-mercaptoethyl)tetramethyldisilazane (eq 2). Nmr analysis of the product indicated the ratio of $-Me_2SiS-$ to $-Me_2SiHN-$ to be about one, corresponding approximately to a compound such as $HN(SiMe_2CH_2CH_2SSiMe_2CH_2CH_2SH)_2$ (I).



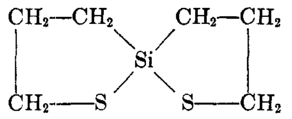
$$2Me_2ClSiCH_2CH_2S\overset{O}{\overset{\|}{C}}CH_3 + \text{excess } NH_3 \xrightarrow{-33^\circ} HN(SiMe_2CH_2CH_2SH)_2 + 2NH_4Cl + 2CH_3\overset{O}{\overset{\|}{C}}NH_2\cdot \quad (2)$$

Product I was used to prepare silylalkanethiols. Compound I with glacial acetic acid formed 2-dimethylacetoxysilylethanethiol and with anhydrous hydrogen chloride I formed 2-dimethylchlorosilylethanethiol. Hydrolysis of an equal molar mixture of I and 2-dimethylacetoxysilylethanethiol gave 2-dimethylhydroxysilylethanethiol. Compound I decomposed at approximately 240° to produce a 77% yield of 1,1,3,3-tetramethyl-1,3-disila-2,4-dithiacyclohexane ($Me_2SiSSiMe_2CH_2CH_2S$). At 175° I gave a polymer having the structure $\text{-}\!\!\!(SiMe_2CH_2CH_2S\text{-}\!\!\!)_x$ and a small amount of the above cyclic compound.

Ammonolysis of bis(3-thiolacetoxypropyl)dichlorosilane gave the unique 1,6-dithia-5-silaspiro[4.4]-nonane (eq 3).

$$Cl_2Si(CH_2CH_2CH_2SAc)_2 \xrightarrow{NH_3} \text{-}\!\!\!(HNSi(CH_2CH_2CH_2SH)_2\text{-}\!\!\!)_x + 2AcNH_2 \quad (3)$$

$$\downarrow \Delta$$



The reaction of vinylsilanes with ethanethiolic acid was investigated further to determine the influence of structure upon the reactivity of vinylsilanes. The results of this study with ethanethiolic acid were then compared with similar results using 1-butanethiol and benzenethiol. The reactivities of compounds of the formula $RR'R''SiCH{=}CH_2$ relative to the reactivity of hexene-1 were determined by permitting each of the vinylsilanes to compete with hexene-1 for an insufficient amount of the thiols. The results of these competitive reactions are shown in Table I.

The reactivity of thiols with vinylsilanes of the formula $RR'R''SiCH{=}CH_2$ is not strongly influenced by the structures of R, R′, and R″. The most reactive vinylsilane was $Me_3SiCH{=}CH_2$; the least reactive was $Cl_3SiCH{=}CH_2$. The difference in reactivity between these was only slightly greater than one order of magnitude. A regular change in the log of the relative rate constant in each series, $Me_nX_{3-n}SiCH{=}CH_2$ was observed which suggested that a linear free energy correlation might be made.

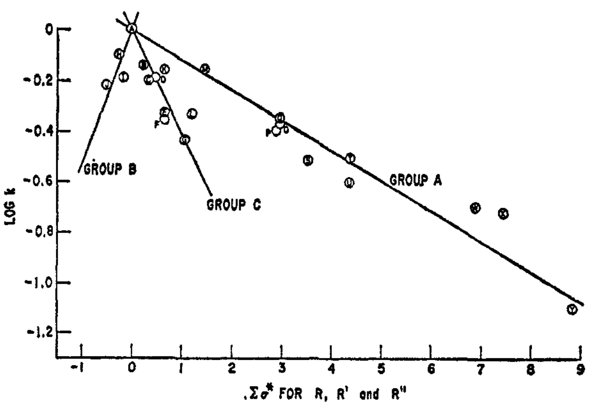


Figure 1.—Log k *vs.* $\Sigma\sigma^*$ for $RR'R''SiCH{=}CH_2 + AcSH \rightarrow RR'R''SiCH_2CH_2CH_2SAc$; rate k relative to $k_{\text{hexene}} = 1$; lettered points refer to compounds shown in Table I.

Table I

Reactivities of $RR'R''SiCH{=}CH_2$ Relative to n-$BuCH{=}CH_2$ = 1 toward Ethanethiolic Acid, Benzenethiol, and n-Butanethiol

	RR′R″	AcSH k/k_0	PhSH k/k_0	BuSH k/k_0
A.	Me_3	1.00	6.8	4.5
B.	$PhCH_2Me_2$	0.73	5.4	
C.	$(F_3CCH_2CH_2)Me_2$	0.63	2.2	
D.	$(PhCH_2)_2Me$	0.64		
E.	$(PhCH_2)_3$	0.47		
F.	$(F_3CCH_2CH_2)_2Me$	0.44		
G.	$ClCH_2Me_2$	0.37		
H.	$Me_3SiCH_2Me_2$	0.80	6.2	
I.	i-$PrMe_2$	0.64	4.7	
J.	$(Me_3SiCH_2)_2Me$	0.60		
K.	$PhMe_2$	0.69	4.0	
L.	Ph_2Me	0.47		
M.	$MeOMe_2$	0.69	3.9	2.8
N.	Me_3SiOMe_2	0.59	3.1	2.7
O.	$(EtO)_2Me$	0.44	2.5	2.6
P.	$(MeO)_2Me$	0.40	2.2	1.8
Q.	$ClMe_2$	0.45		
R.	$(Me_3SiO)_2Me$	0.36	2.4	1.8
S.	$PhClMe$	0.30		
T.	$(EtO)_3$	0.31		
U.	$(MeO)_3$	0.25	1.4	1.3
V.	$(Me_3SiO)_3$	0.21	1.4	1.5
W.	Cl_2Me	0.20		
X.	$PhCl_2$	0.19		
Y.	Cl_3	0.08		

Figure 1 shows the results of an attempt to correlate the data of Table I with a modified form of the Taft equation.[9]

$$\log k/k_{\text{hexene}} = \Sigma\sigma^*\rho^*$$

The correlation shown in Figure 1 is poor. However, vinylsilanes bearing at least one substituent having an unshared electron pair adjacent to silicon seem to correlate reasonably well (group A in Figure 1). Three vinylsilanes (H, I, and J of Table I) form a separate group. They may be displaying steric effects of branching in the isopropyl and trimethylsilylmethyl

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[9] R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, pp 556–675.

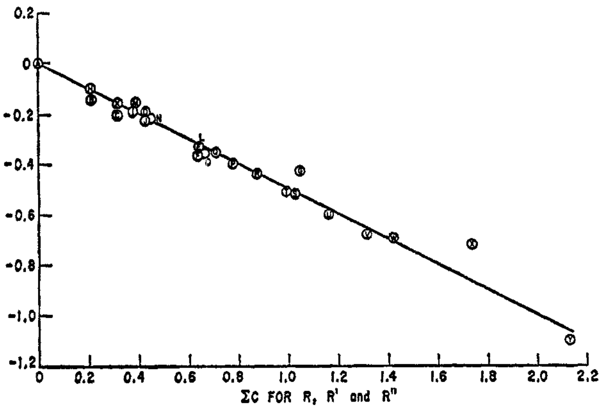

Figure 2.—Log k *vs.* ΣC for RR'R''SiCH=CH$_2$ + AcSH → RR'R''SiCH$_2$CH$_2$SAC; log k = $-0.517C$; lettered points refer to compounds shown in Table I.

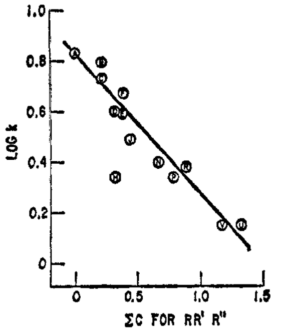

Figure 3.—Log k *vs.* ΣC for RR'R''SiCH=CH$_2$ + PhSH → RR'R''SiCH$_2$CH$_2$SPh; log k = $-0.57C$; lettered points refer to compounds shown in Table 1.

groups. The rates of reaction for the other vinylsilanes correlate with a third line (group C). The compounds of group C have unbranched R groups with no unshared electrons adjacent to silicon. Two vinylsilanes (K and L) have phenyl and methyl substituents and seem to fall midway between groups A and C of Figure 1.

These observations suggested that the modified Taft equation fails to correlate the data of Table I because of steric effects and effects due to dative bonding of groups with unshared or π electrons adjacent to silicon. An empirical constant C for each R group on silicon was found which leads to a correlation with all the relative rate data of Table I. The Taft σ^* value was accepted as C for the methyl (0.0), 3,3,3-trifluoropropyl (0.32), benzyl (0.215), and chloromethyl (1.05) substituents. The value of C for other substituents was then calculated from the equation log $k/k_{\text{hexene}} = -0.517\Sigma C$. By this method the following values were assigned: phenyl, 0.32; chlorine, 0.71; trimethylsiloxy, 0.44; methoxy, 0.39; ethoxy, 0.33; trimethylsilylmethyl, 0.21; and isopropyl, 0.38.

These new values for the substituents on silicon allowed us to make the surprisingly linear correlation shown in Figure 2. The values of C for the three groups on silicon are very nearly additive and the sum of the three values apparently represents the total of inductive, steric, and dative bonding effects of substituents on silicon for the addition of ethanethiolic acid to the vinyl group. The values of C obtained in this way were found to be equally useful to correlate relative reactivities with benzenethiol and 1-butanethiol. These correlations are shown in Figures 3 and 4.

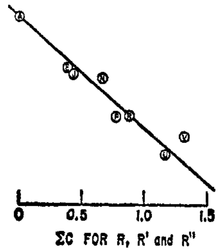

Figure 4.—Log k *vs.* ΣC for RR'R''SiCH=CH$_2$ + *n*-BuSH → RR'R''SiCH$_2$CH$_2$S-Bu-*n*; log k = $-0.46C$; lettered points refer to compounds shown in Table I.

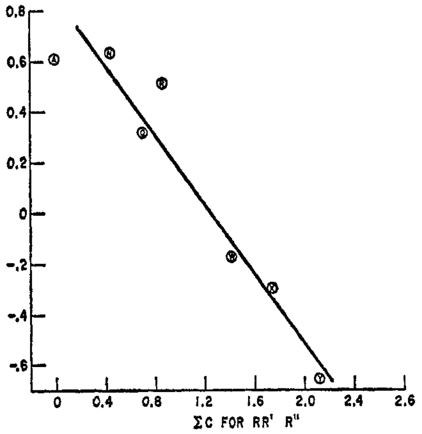

Figure 5.—Log kv s. ΣC for RR'R''SiCH=CH$_2$ + MeHSiCl$_2$ → RR'R''SiCH$_2$CH$_2$SiMeCl$_2$; log k = $0.69C$; lettered points refer to compounds in Table I.

Data for the rates of reaction of a series of RR'R''SiCH=CH$_2$ compounds could be found only for one other reaction. These data were gathered by M. C. Musolf in this laboratory some time ago. He studied the relative rates of RR'R''SiCH=CH$_2$ relative to *n*-hexene-1 in the addition of MeCl$_2$SiH catalyzed by chloroplatinic acid.[10] In his study an insufficient amount of MeCl$_2$SiH and an equimolar mixture of RR'R''SiCH=CH$_2$ and hexene-1 reacted in the presence of a trace of chloroplatinic acid. The ratio of the two products RR'R''SiC$_2$H$_4$SiCl$_2$Me and *n*-HexMeSiCl$_2$ was determined by vpc and the relative rates were calculated. The calculation was carried out by the method described in the Experimental Section for the thiols.

The platinum-catalyzed addition of silicon hydrides to aliphatic double bonds has been studied intensively. Reactions such as the above seem to be examples of homogeneous catalysis which give rise to platinum–olefin–silane complexes as highly reactive intermediates during the formation of adducts.[11] Although the mechanisms of free-radical addition of thiols and the platinum-catalyzed addition of silicon hydrides to vinylsilanes seem to be quite different, Musolf's kinetics correlate fairly well with the ΣC values. (See Figure 5.)

These correlations are sufficiently good and apply to such a variety of R groups on silicon that more examples of kinetic data or other kinds of data for series of silicon compounds would be valuable to assist in an

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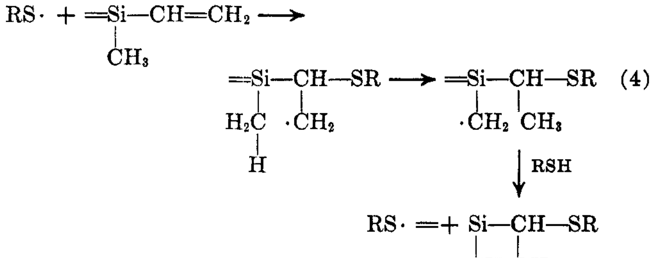
(10) M. C. Musolf, private communication,.

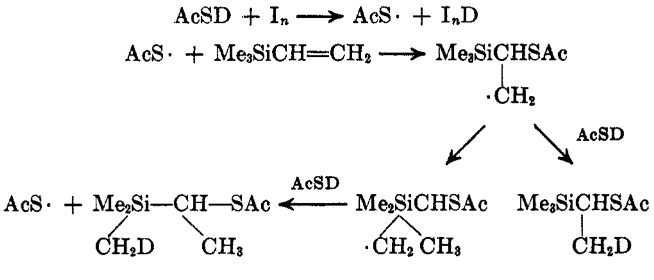
(11) (a) A. J. Chalk and J. F. Harrod, *J. Amer. Chem. Soc.*, **87**, 16 (1965). (b) J. W. Ryan and J. L. Speier, *ibid.*, **86**, 895 (1964).

estimation of how generally valid these C values may be.

The free-radical addition of thiols to α-olefins leads only to terminal products.[12] Wetterlin[8] found only the terminal adduct from benzenethiol and trimethylvinylsilane when he used trimethylbenzylammonium hydroxide as a catalyst in the presence of hydroquinone. We found that vinyltrimethoxysilane and ethanethiolic acid did not react in the presence of hydroquinone and *p*-toluenesulfonic acid. All evidence seems to indicate that the vinylsilanes are unique in forming nonterminal adducts with thiols and that only those silanes with alkyl, alkoxy, or trimethylsiloxy groups on the silicon gave the nonterminal adduct. The suggestion arose that perhaps an unusual shift of hydrogen might be occurring in the intermediate radical (eq 4). This postulate was proved incorrect by allowing ethanethiolic acid-*d* to react with trimethylvinylsilane (Scheme I). Nmr showed the nonterminal adduct to be $Me_3SiCH(CH_2D)SAc$. Therefore, the intermediate must be $Me_3SiCH(\dot{C}H_2)SAc$. The terminal adduct was the expected $Me_3SiCHDCH_2$-SAc.



SCHEME I



The yield of nonterminal adduct is dependent on the substituents on silicon, see Table II. Replacing a methyl group of trimethylvinylsilane with a methoxy, ethoxy, or 3,3,3-trifluoropropyl group does not change the yield of nonterminal adduct significantly. However, a significant decrease in the yield of nonterminal adduct is observed when two methyl groups are replaced by these groups. Replacing only one methyl group with a chlorine atom also reduces the yield of nonterminal adduct significantly. Only a slight change was observed when all the methyl groups were replaced with trimethylsiloxy groups. No correlation between the yield of nonterminal adduct and the relative reactivity of the vinylsilane was observed.

TABLE II

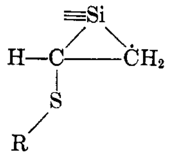
YIELD OF NONTERMINAL ADDUCT FROM THE REACTION OF ETHANETHIOLIC ACID WITH VINYLSILANES

Vinylsilane	% yield by glpc
Me_3Si-	10.0
$Me_2F_3CCH_2CH_2Si$-	10.3
Me_2MeOSi-	9.6
Me_2Me_3SiOSi-	9.5
$Me(Me_3SiO)_2Si$-	8.7
$(Me_3SiO)_3Si$-	7.6
$Me(F_3CCH_2CH_2)Si$-	5.3
$Me(EtO)_2Si$-	5.0
$(EtO)_3Si$-	5.4
$(MeO)_3Si$-	5.2
$Me(Me_3SiCH_2)_2Si$	5.2
Me_2ClSi-	1.3
$MeCl_2Si$-	1.1
Cl_3Si-	0.0

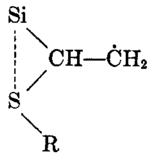
Wetterlin[8] proposed that the nonterminal adduct was formed because of dπ–pπ bonding between the empty d orbitals of silicon and the π electrons of the double bond (eq 5). This effect should increase the electron

$$Me_3SiCH{=}CH_2 \longleftrightarrow Me_3\overset{-}{Si}{=}CH\overset{+}{C}H_2 \qquad (5)$$

density of the carbon adjacent to silicon enhancing attack on this carbon by the electrophilic thiol radical. The $\equiv SiCH(SR)CH_2\cdot$ radical may be somewhat stabilized by neighboring group effects of silicon and sulfur similar to that proposed by Readio and Skell.[13]



Or this intermediate could be stabilized by interaction of the nonbonding electrons on sulfur with the d orbitals of silicon.



These types of interaction might be responsible for nonterminal adducts of some vinylsilanes.

Experimental Section

Nuclear magnetic resonance (nmr) spectra were obtained in CCl_4 on a Varian Model A-60 spectrometer using tetramethylsilane as the standard. Infrared spectra were obtained with a Perkin-Elmer Model 221 spectrometer. Gas-liquid partition chromatography (glpc) spectra were obtained with an F & M Model 720 instrument. The columns were 4 or 6 ft lengths of 0.25-in. stainless steel tubing packed with Dow Corning FS 1265 Gum on Chromosorb P (80–100 mesh). The Chromosorb P had been treated with hexamethyldisilazane.

Reagents. **Ethanethiolic acid** was prepared by the method of Ellingboe[14] in 80% yield.

Acetyl sulfide (bp, 75–76° (40 mm), n^{25}D 1.4805) was prepared in 71% yield by the method of Bonner.[15]

Ethanethiolic acid-*d* was prepared by allowing a mixture of acetyl sulfide (70 g, 0.5 mol), deuterium oxide (10 g, 0.5 mol), and anhydrous sodium acetate (0.05 g, 0.0006 mol) to react at room temperature for 6 days in a nitrogen atmosphere. The mixture was stripped from the catalyst under reduced pressure. The distillate was fractionated to give 32.7 g (87% yield) of ethanethiolic acid-*d:* bp 42–45° (160 mm); n^{25}D 1.4613. Infrared analysis indicated the product to be about 91% ethanethiolic acid-*d*, 3% ethanethiolic acid, and 6% deuterium oxide.

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[12] W. A. Hewett, Doctoral Dissertation Series, Publ. No. 15134.

[13] P. D. Readio and P. S. Skell, *J. Org. Chem.*, **31**, 759 (1966).

[14] E. K. Ellingboe in "Organic Synthesis," Coll. Vol. IV, N. Rabjohn, Ed., John Wiley and Sons, Inc., New York, N. Y., 1963, p 928.

[15] W. Bonner, *J. Amer. Chem. Soc.*, **72**, 427 (1950).

TABLE III

NEW COMPOUNDS

	Compd[a]	Bp, °C (mm)	n^{25}_{D}	d^{25}_{4}	Anal. Found (calcd), %	Neut equiv Found (calcd)
1.	$ClCH_2Me_2SiVi$	119–120	1.4382	0.896		
2.	$Me_2MeOSiVi$	82	1.3920	0.797	—CH=CH₂, 23.4 (23.2); MeO—, 26.4, 26.5 (26.6)	
3.	$Me(MeO)_2SiVi$	104	1.3920	0.884	Si, 21.0 (21.2)	
4.	$Me_2(F_3CCH_2CH_2)SiVi$	113–115	1.3765	0.968	Si, 14.9 (15.4); F, 32.1 (31.2); C, 46.4 (46.2); H, 7.5 (7.2)	
5.	$Me(F_3CCH_2CH_2)_2SiVi$	105 (105)	1.3725	1.130	Si, 11.8 (10.6); F, 42.2 (43.2); C, 41.1 (40.9); H, 5.3 (5.3)	
6.	$Me(Me_3SiCH_2)_2SiVi$	113 (30)	1.4511	0.813	Si, 34.9 (34.4); C, 54.4 (54.1); H, 11.9 (11.5)	
7.	$Me(PhCH_2)_2SiVi$	141 (0.3)	1.5628	0.989	Si, 11.0 (11.1); C, 81.4 (80.8); H, 8.3 (8.0)	
8.	$Cl_3SiCH_2CH_2SAc$	63–66 (1)	1.4940	1.320	Si, 11.8 (11.8); S, 13.6 (13.5)	78.9 (79.2)
9.	$MeCl_2SiCH_2CH_2SAc$	93–94 (8)	1.4898	1.210	Si, 12.9 (12.9); S, 14.3 (14.8)	107 (108.6)
10.	$Me_2ClSiCH(CH_3)SAc$	95–97 (21)	1.4782	1.064	Si, 14.1 (14.3); S, 16.5 (16.3)	194 (196.8)
11.	$Me_2ClSiCH_2CH_2SAc$	101–102 (13)	1.4802	1.069	Si, 14.3 (14.3); S, 17.3 (16.3)	196 (196.8)
12.	$Me_3SiCHDCH_2SAc$	99–100 (30)				
13.	$Me_3SiCH(CH_2D)SAc$	90–95 (35)				
14.	$Me_3SiCH(CH_3)SAc$	81–82 (22)	1.4642	0.927	Si, 15.3 (15.9); S, 18.3 (18.2)	
15.	$Me(MeO)_2SiCH_2CH_2SAc$	75 (1)	1.4579	1.053	Si, 13.8 (13.5); S, 15.2 (15.4)	
16.	$(MeO)_3SiCH(CH_3)SAc$	67–69 (5)	1.4502	1.100	Si, 12.5 (12.5); S, 14.4 (14.4)	
17.	$(MeO)_3SiCH_2CH_2SAc$	95 (5)	1.4512	1.105	Si, 12.3 (12.5); S, 13.9 (14.4)	
18.	$(AcO)_3SiCH_2CH_2SAc$		1.4596	1.219	Si, 9.1 (8.7); S, 10.7 (10.4)	
19.	$Cl_2Si(CH_2CH_2CH_2SAc)_2$	dec	1.5208	1.208	Si, 8.1 (8.4); S, 19.6 (19.2); Cl, 19.1 (21.5)	
20.	$(Me_3SiO)_3SiCH_2CH_2SAc$		1.4270	0.941	Si, 28.1 (28.2); S, 8.0 (8.0)	
21.	$(MeO)_3SiCH_2CH_2SH$	108 (50)	1.4382	1.069	Si, 15.5 (15.4); S, 17.6 (17.6)	
22.	$Me(MeO)_2SiCH_2CH_2SH$	96–98 (50)	1.4462	1.008	Si, 16.7 (16.9); S, 18.7 (19.3)	
23.	$Me_2MeOSiCH_2CH_2SH$	71 (18)	1.4515	0.934		*b*
24.	$Me_2ClSiCH_2CH_2SH$	53 (5)	1.4754	1.027	Si, 18.1 (18.1); S, 20.7 (20.7); Cl, 22.8 (22.9)	
25.	$Me_2AcOSiCH_2CH_2SH$	67–71 (2.5)	1.4556	1.010	Si, 15.9 (15.8); S, 17.8 (18.0)	
26.	$Me_2HOSiCH_2CH_2SH$		1.4742	0.986	Si, 20.3 (20.6); S, 23.0 (23.5)	
27.	$Me_2SiSSiMe_2CH_2CH_2S$	120 (30)	1.5295	1.030	Si, 26.7 (26.9); S, 30.2 (30.7)	
28.	$(Me_2SiCH_2CH_2S)_x$		1.5515		Si, 24.1 (23.8); S, 27.3 (27.1)	
29.	$S(CH_2)_3Si(CH_2)_3S$	85–90[c] (1.0)			Si, 15.4 (15.9); S, 36.1 (36.3)	

[a] Registry no. in descending order are 1, 16709-86-7; 2, 16546-47-7; 3, 16753-62-1; 4, 683-29-4; 5, 16709-89-0; 6, 16709-90-3; 7, 16709 91-4; 8, 16709-92-5; 9, 16709-93-6; 10, 16709-94-7; 11, 16709-95-8; 12, 16720-18-6; 13, 16709-96-9; 14, 16709-97-0; 15, 16709-98-1; 16 16709-99-2; 17, 16720-19-7; 18, 16710-00-2; 19, 16710-01-3; 20, 16710-02-4; 21, 7538-45-6; 22, 14857-98-8; 23, 16710-05-7; 24, 16710-06-8; 25, 16710-64-8; 26, 16710-65-9; 27, 16704-34-0; 29, 16704-32-8. [b] Mercaptan equiv was 150.1 (calcd 150.3). [c] Mp 26–28°.

The S–D (1873 cm^{-1}) and S–H (2580 cm^{-1}) stretching absorptions were used for the analysis. The nmr spectrum showed only one peak at τ 7.64 ($CH_3C(=O)$).

Preparation of Vinylsilanes. Chloromethyldimethylvinylsilane was prepared by adding a slight excess of vinyllithium (Alpha Inorganics, Inc.) to a solution of chloromethyldimethylchlorosilane (163 g, 1.14 mol) in tetrahydrofuran (1000 ml). The mixture was refluxed overnight, distilled free of solvent, and extracted with pentane. The extracts were distilled to give 93.5 g (67% yield) of chloromethyldimethylvinylsilane. The material was judged to contain less than 2% impurities by glpc analysis. Its nmr spectrum showed a characteristic vinyl group absorption at τ 3.7–4.4, (2.9 protons), a singlet at 7.27 (CH_2Cl) (2.0 protons) and a singlet at 9.81 (Me_2Si) (6.1 protons). The physical properties are given in Table III, compound 1.

Dimethylvinylmethoxysilane was prepared in 77% yield from dimethylvinylchlorosilane and trimethylorthoformate by the method of Shorr.[16] Properties and analyses are given in Table III, compound 2.

Methylvinyldimethoxysilane was prepared in 46% yield by treating methylvinyldichlorosilane with methanol. Properties and analyses are given in Table III, compound 3.

3,3,3-Trifluoropropylvinyldimethylsilane was prepared by adding a mixture of dimethylvinylchlorosilane (120.7 g, 1.0 mol) and 1,1,1-trifluoro-3-bromopropane (177 g, 1.0 mol) to magnesium (24.3 g, 1.0 g-atom) in ether (300 ml). The mixture was washed with dilute hydrochloric acid and distilled to obtain 48.4 g (24%) of product having the properties and analyses given in Table III, compound 4.

Bis(3,3,3-trifluoropropyl)vinylmethylsilane was prepared from methylvinyldichlorosilane (141 g, 1.0 mol) and 3,3,3-trifluoropropylmagnesium bromide, prepared from 1,1,1-trifluoro-3-bromopropane (390 g, 2.2 mol) and magnesium (53 g, 2.2 g-atom) in ether (600 ml). Ether was removed until the pot temperature reached 70° before any reaction was observed. The usual work-up with dilute hydrochloric acid gave 97 g (37% yield) of bis(3,3,3-trifluoropropyl)methylvinylsilane. Properties and analyses are given in Table III, compound 5.

Bis(trimethylsilylmethyl)methylvinylsilane was prepared by heating a mixture of methylvinyldichlorosilane (64.5 g, 0.5 mol) and trimethylsilylmethylmagnesium chloride, prepared from chloromethyltrimethylsilane (122.6 g, 1.0 mol), magnesium (24.3 g, 1.0 g-atom), and ether (800 ml) at reflux overnight. The usual work-up with dilute hydrochloric acid gave 26 g of crude product. This material was purified with activated alumina (100 g) to give 15 g (12% yield) of methylbis(trimethylsilylmethyl)vinylsilane. Properties and analyses are given in Table III, compound 6. Impure trimethylsilylmethylmethylvinylsilanol and *sym*-bis(trimethylsilylmethyl)dimethyldivinyldisiloxane were also isolated. These were identified by nmr and infrared analyses.

Dibenzylmethylvinylsilane was prepared from methylvinyldichlorosilane (64.5 g, 0.5 mol) and benzylmagnesium chloride, prepared from benzyl chloride (127.9 g, 1.05 mol), magnesium (24.3 g, 1.0 g-atom), and ether (750 ml). The usual work-up with dilute hydrochloric acid gave 98 g (78% yield) of dibenzylmethylvinylsilane. Properties and analyses are given in Table III, compound 7.

Preparation of Silylethyl Ethanethiolates. 1-Trimethoxysilylethyl ethanethiolate and 2-trimethoxysilylethyl ethanethiolate were prepared by dripping a mixture of ethanethiolic acid (420 g, 5.5 mol) and azobisisobutyronitrile (4.1 g, 0.025 mol) into vinyltrimethoxysilane (740 g, 5.0 mol) at 80–90° with irradiation from an ultraviolet lamp. After 1 hr the mixture was distilled to give 687 g of pure 2-trimethoxysilylethyl ethanethiolate. Properties are given in Table III, compound 17. A

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(16) L. M. Shorr, *J. Amer. Chem. Soc.*, **76**, 1390 (1954).

sample of pure 1-trimethoxysilylethyl ethanethiolate was obtained by redistilling the lower boiling fractions. Properties and analyses are given in Table III, compound 16. The ratio of terminal adduct to nonterminal adduct was 95:5 by glpc. The over-all yield of trimethoxysilylethyl ethanethiolates was 954 g (85%).

Air or various peroxides were effective initiators for this reaction. The silylethyl ethanethiolates listed in Table III were prepared from the appropriate vinylsilanes and ethanethiolic acid by procedures similar to the above. The reaction proceeds smoothly only with freshly distilled ethanethiolic acid. The order of mixing the reagents does not appear to affect the reaction. In the preparation of bis(3-thiolacetoxypropyl)dichlorosilane, the diallyldichlorosilane was added to excess ethanethiolic acid.

Preparation of Silylalkanethiols. Base-Catalyzed Methanolysis of 2-Trimethoxysilylethyl Ethanethiolate.—A solution of 2-trimethoxysilylethyl ethanethiolate (95 g, 0.42 mol), methanol (81 ml, 2.0 mol), and sodium (0.1 g, 0.004 g-atom) was refluxed 2 hr and distilled to give 71 g (93% yield) of 2-trimethoxysilylethanethiol. Properties and analyses are given in Table III, compound 21. 2-Dimethylmethoxysilylethanethiol and 2-methyldimethoxysilylethanethiol were prepared in similar manner in 85 and 71% yields, respectively.

Acid-Catalyzed Methanolysis of 2-Trimethoxysilylethyl Ethanethiolate.—A solution of 2-trimethoxysilylethyl ethanethiolate (5.6 g, 0.025 mol), methanol (1.02 g, 0.03 mol), and *p*-toluenesulfonic acid (0.02 g, 0.0001 mol) was refluxed 96 hr. Glpc indicated only 65% conversion of ethanethiolate into thiol.

Ammonolysis of 2-Dimethylchlorosilylethyl Ethanethiolate.—2-Dimethylchlorosilylethyl ethanethiolate (767.0 g, 3.9 mol) was added dropwise to liquid ammonia (1,310 ml, 63 mol). The mixture was stirred for 13 hr at −33° under nitrogen. Hexane (300 ml) was added and the excess ammonia was allowed to escape. A clear liquid and a solid cake of ammonium chloride and acetamide were obtained. The liquid was decanted from the solid and concentrated at room temperature under reduced pressure to give 443 g (80% yield) of crude product (I). Nmr analysis indicated that 40% of the methyl groups were on a silicon attached to sulfur (τ 9.92). The infrared spectrum showed the following absorptions: $\lambda_{max}^{CCl_4}$ 3370 (m) N–H, 2580 (w) SH; $\lambda_{max}^{CS_2}$ 930 (s) SiNHSi.

Anal. Calcd for $C_8H_{23}NS_2Si_2$: Si, 22.1; S, 25.2; N, 5.5. Found: Si, 22.1; S, 25.3; N, 3.5.

2-Dimethylchlorosilylethanethiol was prepared by saturating a solution of the above product I (25.4 g, ~0.1 mol) and hexane (50 ml) with hydrogen chloride. The mixture was filtered free of ammonium chloride and distilled to give 16.4 g (53% yield) of 2-dimethylchlorosilylethanethiol. Properties and analyses are given in Table III, compound 24.

2-Dimethylacetoxysilylethanethiol was prepared by adding acetic acid (18.5 ml, 0.32 mol) to a solution of I (26.9 g, ~0.11 mol) and hexane (25 ml). The mixture was filtered free of ammonium acetate and distilled to give 24.0 g (67% yield) of 2-dimethylacetoxysilylethanethiol. Properties and analyses are given in Table III, compound 25.

2-Dimethylhydroxysilylethanethiol was prepared by adding a solution of 2-dimethylacetoxysilylethanethiol (5.34 g, 0.03 mol) and I (7.6 g, ~0.03 mol) to 5% aqueous ammonium acetate (50 ml). After stirring the mixture for about 1 hr at room temperature hexane (10 ml) was added and two liquid phases formed. The organic phase was washed with distilled water (10 ml) and concentrated at room temperature under reduced pressure to give 9.1 g (86% yield) of 2-dimethylhydroxysilylethanethiol. Its nmr and infrared spectra indicated only traces of water and disiloxane present. Properties and analyses are given in Table III, compound 26.

1,1,3,3-Tetramethyl-1,3-disila-2,4-dithiacyclohexane was prepared by heating I (40.0 g, ~0.16 mol) at 240° (30 mm) until the pot was dry. The distillate was fractionated to give 28 g (77% yield) of 1,1,3,3-tetramethyl-1,3-disila-2,4-dithiacyclohexane. Properties and analyses are given in Table III, compound 27.

$-\!(SiMe_2CH_2CH_2S)\!-$ was prepared by heating I (50 g, 0.2 mol) at 175° (3 mm) for 48 hr to give 32 g (68% yield) of polymer, viscosity 3700 cSt. Properties and analyses are given in Table III, compound 28. A 10% yield of 1,1,3,3-tetramethyl-1,3-disila-2,4-dithiacyclohexane was obtained also.

Reactions of Thiols and Ethanethiolic Acid with Vinylsilanes. Ethanethiolic Acid-*d* with Trimethylvinylsilane.—Ethanethiolic acid-*d* (14.5 ml, 0.183 mol) was added dropwise to a solution of trimethylvinylsilane (22 g, 0.22 mol) and Lupersol-11 (0.15 g, 0.001 mol) at 50–80°. The mixture was distilled to give 29.6 g (92% yield) of product. Pure nonterminal adduct was obtained by preparative glpc. Pure terminal adduct was obtained from the distillation. The nmr spectrum showed the nonterminal adduct to be $Me_3SiCH(CH_2D)SC({=}O)CH_3$ with singlet peaks at τ 9.88 (Si–CH_3*) and 7.69 ((O=)C—CH_3*), a triplet peak at 7.21 (SiCH*S), and a doublet peak at 8.72 ($CHCH_2$*D). The proton ratios were 8.7:3.0:2.1:1.0, respectively. The nmr spectrum of the terminal adduct showed it to be $Me_3SiCHDCH_2SC({=}O)CH_3$ with singlet peaks at τ 9.95 (Si–CH_3) and 7.78 ((O=)CCH_3), a doublet peak at 7.19 (SCH_2), and a complex peak at 9.18 (SiCHD). The proton ratios were 8.9:3.0:1.9:1.2, respectively.

Nonterminal Adducts from the Reaction of Ethanethiolic Acid with Vinylsilanes.—Ethanethiolic acid (0.5 *M* in benzene) was allowed to react with a slight excess of a vinylsilane at 40 ± 0.5°. The reaction was initiated with about 1 mol % Lupersol-11. The reaction mixture was analyzed for the relative amounts of terminal and nonterminal adducts by glpc. The results are given in Table II.

Relative Reactivities of Vinylsilanes toward Thiols and Ethanethiolic Acid.—Ethanethiolic acid (~0.01 mol) was added in 0.1-ml portions to a solution of hexene-1 (~0.01 mol) and vinylsilane (0.01 mol) in ethylbenzene (10 ml) at 40° in a 2-oz vial. The reaction was initiated with one drop of Lupersol-11. After each addition an exothermic reaction was observed. The reaction mixture was cooled by removing the vial from the bath. Glpc indicated complete reaction a few minutes after the ethanethiolic acid was added. A sample of the original vinylsilane, hexene-1, and ethylbenzene solution was analyzed by glpc and a factor for converting area of the olefin into moles of olefin was obtained (eq 6). A sample of the reaction mixture was analyzed by glpc

$$Z = \frac{\text{(area of olefin)}}{\text{(moles of olefin) (area of ethylbenzene)}} \tag{6}$$

and the amount of unreacted olefin was obtained as in eq 7.

$$\text{moles of unreacted olefin} = \frac{\text{(area of unreacted olefin)}}{(Z)\ \text{(area of ethylbenzene)}} \tag{7}$$

The relative rate (k/k_0) was calculated using the following formula.

$$k/k_0 = \frac{\ln\text{ (moles of unreacted vinylsilane/moles of initial vinylsilane)}}{\ln\text{ (moles of unreacted hexene-1/moles of initial hexene-1)}} \tag{8}$$

The studies with benzenethiol and 1-butanethiol were carried out using the same procedure except the reactions were not exothermic and did not require cooling. The reaction times were about 16–20 hours. No effect on the reactivities of various vinylsilanes was observed when benzene was used as the solvent instead of ethylbenzene. Benzene was used in place of ethylbenzene whenever the retention times of the vinylsilane and ethylbenzene were the same. Hexene-1 and octene-1 were found to react at the same rate. Octene-1 was used instead of hexene-1 whenever hexyl ethanethiolate and the vinylsilane had the same retention times. Several vinylsilanes were allowed to compete with each other to check if the reaction was really competitive. In each case the observed reactivities agreed well with the predicted value obtained from the competition reactions with hexene-1. The approximate range of experimental error was found to be about 10%. Usually the several determinations were well within this range. The results are given in Table I.

Relative Reactivities of Vinylsilanes toward Methyldichlorosilane.—Methyldichlorosilane (1 ml, 0.01 mol), hexene-1 (0.01 mol), the vinylsilane (0.01 mol), and chloroplatinic acid (5 × 10^{-7} mol) were sealed in 10 mm × 250 mm Pyrex tubes and heated overnight in a boiling water bath. The tubes were opened and the contents were analyzed by glpc methods. The relative reactivity of each vinylsilane was calculated as in the preceding section. The following reactivities were observed (relative to hexene-1): Me_3SiVi, 4.04; $Me_2ClSiVi$, 2.05; $MeCl_2SiVi$, 0.67; Cl_3SiVi, 0.159; $(Me_3SiO)Me_2SiVi$, 4.29; $(Me_3SiO)_2MeSiVi$, 3.24; $C_6H_5Cl_2SiVi$, 0.502.

Registry No.—Ethanethiolic acid-*d*, 16704-33-9; I, 16808-49-4.

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Optical Purity and Optical Rotatory Power of Dehydronorcamphor[1a]

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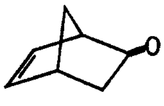
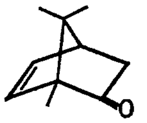
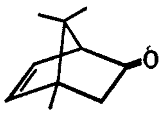
The optical properties of dehydronorcamphor have been reinvestigated. The previously reported absolute rotation and ORD amplitude of the $n \rightarrow \pi^*$ transition have been confirmed by an independent determination of the optical purity by nmr spectroscopy. The circular dichroism has been found to match closely the corresponding values reported for the $n \rightarrow \pi^*$ transition of dehydrocamphor and dehydroepicamphor.

Bicyclo[2.2.1]hept-5-en-2-one (dehydronorcamphor, **1**) a simple archetype of the dissymmetric β,γ-unsaturated carbonyl chromophore, figures as a key compound in studies of the relationship between optical rotatory power and chemical structure, both from the theoretical[2] and the experimental[3-6] points of view.

It is therefore of interest to note that while (+)-**1** and dehydrocamphor [(−)-**2**] are reported to have similar molecular amplitudes for the Cotton effect of their lowest lying $n \rightarrow \pi^*$ transition (a +780 ± 40[4] and *ca.* −840,[7] respectively), corresponding to similar extinction coefficients [ϵ 277 (λ_{max} 307.5 mμ) and 308 (λ_{max} 304 mμ) for **1**[2a] and **2**[6]], the corresponding molecular ellipticites are reported to differ significantly ($[\theta]_{max}$ $+3.18 \times 10^4$ and -5.89×10^4 for **1**[5] and **2**,[6] respectively). This result is contrary to expectations since, even taking into account that the values cited for **1** and **2** refer to different solvents (hydrocarbon and ethanol, respectively), **1** and **2** do have similar chromophoric geometries and the rotational strengths should clearly manifest parallel behavior in ORD and CD.[2] In terms of the semiquantitative expression relating molecular amplitude and circular dichroism of ketones,[8] $[\theta]_{max}$ values of +6.4 and -6.9×10^4 might have been predicted from the a values of **1** and **2**, respectively, or, conversely, a values of +390 and −720 might have been predicted from the reported $[\theta]_{max}$ values of **1** and **2**, respectively. Whereas calculated and reported values for a and $[\theta]_{max}$ of **2** are in reasonable agreement, the corresponding values for **1** are grossly mismatched.


(+)-1


(−)-2


(+)-3

Similar considerations were advanced by Bays, Cookson, and MacKenzie who pointed out that, given the similarity in the extinction coefficients of the lowest $n \rightarrow \pi^*$ transition of **1**, **2**, and dehydroepicamphor (**3**) [ϵ 325 (λ_{max} 310 mμ)], and given the roughly linear relationship of extinction coefficients (log ϵ) to optical rotatory power (log a or log $\Delta\epsilon$) of ketones,[9] the $\Delta\epsilon_{max}$ values in the CD curves of **1**–**3** would be expected to be closely similar. In fact, reported values for $\Delta\epsilon_{max}$ in hydrocarbon solvents are +9.6, −18.5, and +19.9 for **1**,[5] **2**,[6] and **3**,[6] respectively, once again identifying **1** as the source of the discrepancy. However, because of the close agreement in $\Delta\epsilon_{max}$ values of **2** and **3**, it is the reported circular dichroism of **1** to which the finger of suspicion points, the more so since the $\Delta\epsilon_{max}$ value of **1** calculated[6,8] from the published[4] ORD amplitude is +19.4.

To resolve this discrepancy, we have reinvestigated the ORD and CD of **1**.

Compound **1** was prepared as previously described, *i.e.*, by asymmetric hydroboration of norbornadiene to *exo*-dehydronorborneol (**4**), followed by oxidation to **1**. Use of (−)-α-pinene in the asymmetric hydroboration gave the enantiomer (*i.e.*, (−)-**1**) of the previously studied[4,5] sample.

Since the asymmetric hydroboration furnishes optically impure material, it is crucial to obtain an accurate measure of the optical purity of **1** for purposes of comparison with **2** and **3**, which are obtained from natural sources and are presumed to be optically pure. The optical purity of **1** had previously been estimated[4] by relating **4** and the derived (+)-**1** to *exo*-norborneol, whose optical purity had been established by the isotope dilution method.[10] To be doubly sure, the optical purity of **1** was established in the present work by an entirely independent method, *i.e.*, by nuclear magnetic resonance spectroscopy.[11]

Reaction of racemic dehydronorborneol (*exo*/*endo* ratio 87:13) with an equimolar amount of racemic O-methylmandelyl chloride gave a mixture of esters whose nmr spectrum at 60 MHz in benzene solution showed

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(8) Reference 3b, p 19, gives $a = 0.0122[\theta]_{max}$; $a = 40.28$ ($\Delta\epsilon_{max}$).

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