Preparation and Spectroscopic Properties of Some New Asymmetric Organosilanes

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Partial reduction of a number of racemic methoxysilanes by a chiral reducing complex of lithium aluminium hydride and a terpene alcohol or alkaloidal alcohol has been used to achieve a kinetic resolution. By this means several new optically active silanes and methoxysilanes have been prepared. Indications have been obtained that the stereochemistry of some reactions reported may differ from that of similar reactions recorded in the literature. The o.r.d. and c.d. spectra of the compounds prepared have been recorded, and the potential value of high-resolution n.m.r. spectroscopy in configurational studies on chiral organosilanes has been demonstrated.

THE work of Sommer *et al.* has made available a large number of optically active organosilicon compounds with a reactive functional group on silicon. Stereochemical studies [1] with these compounds have revealed details of mechanism not easily available by other means, and general patterns have become apparent in the stereochemistry of reactions of 1-naphthylphenylmethylsilane and closely related compounds. It has been shown,[2] however, that where the optically active system is markedly different there may be a change in the stereochemistry of some substitution reactions at silicon. For this reason, and for reasons of general utility, it seemed desirable to have available methods of preparing new asymmetric organosilicon systems.

Asymmetric synthesis and kinetic resolution have long been known and studied in organic chemistry [3] but there are few examples of the use of these techniques in organometallic chemistry. The present paper describes the application of kinetic resolution to the preparation of some new asymmetric organosilanes in sufficiently high optical purity to permit their use for stereochemical studies. The initial work [4] on the reduction of (±)-1-naphthylphenylmethylmethoxysilane [(±)-(Ia)] with a complex of lithium aluminium hydride and (+)-quinidine has already been reported. In this experiment there is a difference in the rate of reduction of the two enantiomers by the chiral reducing complex, so that if the reduction is taken only part way both the silane produced and the

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[1] L. H. Sommer 'Stereochemistry, Mechanism and Silicon,' McGraw-Hill, New York, 1965.

[2] R. J. P. Corriu and J. P. Masse, *Tetrahedron Letters*, 1968, 5197.

[3] V. Prelog, *Bull. Soc. chim. France*, 1956, 987; D. R. Boyd and M. A. McKervey, *Quart. Rev.*, 1968, 95.

[4] A. Holt, A. W. P. Jarvie, and G. J. Jervis, *Tetrahedron Letters*, 1968, 4087.

unchanged methoxysilane are optically active. The results of a more extensive series of reductions using complexes of lithium aluminium hydride and alkaloids are shown in Table 1.

$MeSiR^1R^2R^3$

	R^1	R^2	R^3
	Series (a)		
(I)	1-Np	Ph	MeO
(II)	Et	Ph	MeO
(III)	$PhCH_2$	Ph	MeO
(IV)	Mes	Ph	MeO
(V)	Pr^i	Ph	MeO
(VI)	c-Hex	Et	MeO
	Series (b) R^3 = H throughout		
(VII)	1-Np	Ph	Menth $(S)_{Si}$ compd.
(VIII)	1-Np	Ph	Menth $(R)_{Si}$ compd.

1-Np = 1-Naphthyl, Mes = mesityl, c-Hex = cyclohexyl, Menth = (−)-menthoxy.

TABLE 1

Reductions of (±)-1-naphthylphenylmethylmethoxysilane [(±)-(Ia)] with alkaloid–$LiAlH_4$ complexes

Alkaloid *	(1)	(2)	(3)	(4)	(5)	(6)
% Redn.	35	28	33	43	23	27
$[\alpha]_{588}$ † Silane	+1·52°	−0·64°	+1·96°	+1·24°	+0·26°	+4·53°
Purity [a]	4·3	1·8	5·5	3·5	0·7	12·8
$[\alpha]_{588}$ † Methoxysilane	−0·24°	+0·13°	−0·93°	−0·40°	0·00°	−0·86°
Purity [b]	1·4	0·8	5·5	2·4	0·0	5·1

* (1) (−)-quinine, (2) (−)-cinchonidine, (3) (+)-quinidine, (4) (+)-cinchonine, (5) (−)-ephedrine, (6) (+)-ψ-ephedrine.
† Optical activities have been corrected for the optical purity of the alkaloid used.

[a] Optical purity calculated as % of $[\alpha]_D$ +35·5° for the silane. [b] Optical purity calculated as % of $[\alpha]_D$ +17° for the methoxysilane.

TABLE 2

Reductions of (±)-1-naphthylphenylmethylmethoxysilane [(±)-(Ia)] with alcohol–$LiAlH_4$ complexes

Alcohol	(8)	(9)	(10)	(11)	(12)	(13)	(14)
% Redn.	49	56	47	31	24	31	0
$[\alpha]_{588}$ † Silane	+0·71°	+0·34°	0·00°	+0·34°	+0·33°	0·00°	
Purity [a]	2·0	1·0	0	1·0	0·9	0	
$[\alpha]_{588}$ † Methoxysilane	−0·20°	0·00°	0·00°	−0·10°	0·00°	0·00°	
Purity [b]	1·2	0	0	0·6	0	0	

* (8) (−)-menthol, (9) (−)-borneol, (10) (−)-isoborneol, (11) (+)-α-fenchol, (12) (+)-octan-2-ol, (13) cholesterol, (14) lanosterol.
† Optical activities have been corrected for the optical purity of the alcohol used.

a and *b* as in the footnotes to Table 1.

The configuration of carbon atoms C(8) and C(9) in (−)-quinine and (−)-cinchonidine is enantiomeric with that of the corresponding centres in (+)-quinidine and (+)-cinchonine respectively. Clearly the steric results of the asymmetric reductions cannot be related in any simple way to the configurations at these centres in the reducing complex. Noticeable from Table 1, and also from Table 4, is the vast difference in efficiency with which ephedrine and ψ-ephedrine promote asymmetric reduction. This may be attributable to the respective nature of the complexes with lithium aluminium hydride which, as shown by the amount of hydrogen evolved on complex formation, probably involve the NH group as well as the OH group. The preferred conformation of ψ-ephedrine will place the amino- and hydroxy-groups *gauche* to each other so that the complex will be cyclic, whereas in the preferred conformation of ephedrine these groups will be *trans* so that the complex will probably be oligomeric and conformationally less rigid. The higher optical yields obtained using alkaloids compared with terpene alcohols (see below) may similarly be due to the rigidity imposed on the complex by co-ordination of the nitrogen atom of the alkaloid with the aluminium atom. With a view to simplifying the analysis of the results a series of reductions of the methoxysilane (±)-(Ia) with complexes of lithium aluminium hydride with various optically active alcohols were carried out. All these alcohols possessed only one site for complexing and, with the exception of one acyclic alcohol, were conformationally locked. The results are shown in Table 2.

It is clear from Table 2 that the reduction is very sensitive to steric factors, as evidenced by the considerable difference in the reduction rate when lanosterol is used instead of cholesterol. Examination of Courtaulds models shows that the extent of the reaction reflects the magnitude of the steric hindrance exerted on the hydride atoms of the complex by the groups about the hydroxy-bearing carbon atom.

The reaction was then extended to the preparation of optically active silanes with different substituents on the silicon atom. The first of these was phenylethylmethylsilane (IIb). This has been prepared [5] starting from 1-naphthylphenylmethylsilane (Ib) by a preparation which involves four steps. By the asymmetric reduction of (±)-phenylethylmethylmethoxysilane [(±)-(IIa)] the silane (IIb) is obtained in one step with an optical purity of over 40%. Furthermore, there is obtained at the same time the optically active methoxysilane (IIa) whose preparation had not previously been reported. The results of a series of reductions are shown in Table 3.

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[5] L. H. Sommer, K. W. Michael, and W. D. Korte, *J. Amer. Chem. Soc.*, 1967, **89**, 868.

These results further indicate the complex nature of the interactions involved. The reduction with the (−)-quinine complex leads to a silane with the opposite configuration to that from the reduction with the (−)-cinchonidine complex, although the two alkaloids have the same configuration and differ only in the presence of the 6′-methoxy-group in the quinine molecule.

It is interesting to compare the results of the reductions of (Ia) and (IIa). The degree of steric selectivity is much greater for the latter compound than for the former. It is difficult to correlate this with the relative sizes of the groups around the silicon atom in the two cases and it may be connected with the ability of the naphthyl group to co-ordinate with the aluminium atom[6] in the transition state. The results of other asymmetric reactions also suggest that the presence of the naphthyl group may lead to a different transition state topology.

TABLE 3

Reductions of (±)-phenylethylmethylmethoxysilane [(±)-(IIa)] with alkaloid–LiAlH$_4$ complexes

Alkaloid[a]	(1)	(2)	(3)	(4)	(6)
% Redn.[b]	64	51	54	56	34
$[\alpha]_{588}$ Silane	+0·01° [c]	−0·18° [d]	+0·44° [d]	+0·50° [c]	+0·05° [c]
Optical purity	0·5 [f]	7·1 [e]	17·4 [e]	41·2 [f]	4·1 [f]
$[\alpha]_{588}$ Methoxysilane	−0·03°	+0·59°	−1·35°	−3·89°	0·00°

[a] See footnotes to Table 1. [b] Yields based on g.l.c. analysis. [c] $[\alpha]_{588}$ in hexane. [d] $[\alpha]_{588}$ in CCl$_4$. [e] Optical purity calculated as % of $[\alpha]_D$ +2·53° (CCl$_4$). [f] Optical purity calculated as % of $[\alpha]_D$ +1·22° (hexane).

TABLE 4

Reductions of (±) benzylphenylmethylmethoxysilane [(±)-(IIIa)] with alkaloid–LiAlH$_4$ complexes

Alkaloid[a]	(1)	(2)	(3)	(4)	(5)	(6)
% Redn.	47	48	29	42	7	20
$[\alpha]_{588}$ Silane	+1·77°	+3·64°	−1·64°	−7·80°	−0·64	−5·69°
$[\alpha]_{588}$ Methoxysilane	−0·28	−0·86°	+0·16°	+1·86°	+0·00°	+0·46°

[a] See footnote to Table 1.

The high optical yields obtained in the asymmetric reduction of the methoxysilane (IIa) made the method attractive as a possible general route to new optically active organosilanes which were inaccessible by previous methods. Two such systems are benzylphenylmethylsilane and mesitylphenylmethylsilane. Any attempt to prepare these by the method of Sommer might be expected to present problems[7] at the bromodearylation stage. The benzyl group would probably undergo substitution and the mesityl group would be lost by cleavage at this stage. The results of a series of reductions of (±)-benzylphenylmethylmethoxysilane [(±)-(IIIa)] are shown in Table 4. Since this is the first preparation of optically active (IIIa) and (IIIb) there is no means of accurately assessing the optical purity of these products, but the optical activities obtained are quite sufficient to enable the compounds to be used for stereochemical studies. By regarding it as one of an 'isoconfigurational series'[8] the absolute configuration of (+)-(IIIb) may be related to that of (+)-1,2-diphenylpropane,[9] and this silane is hence assigned the *S* configuration. This is supported by o.r.d. and c.d. studies (see below).

In all the reductions reported above, the recovered unchanged methoxysilane had the opposite sign of rotation and the opposite relative configuration to the silane produced. O.r.d. and c.d. spectra (see below) indicated that the silane (−)-(IIIb) had the opposite configuration to the methoxysilane (+)-(IIIa) showing that the reduction had proceeded with retention of configuration. This was confirmed by the reduction of (+)-(IIIa) to (+)-(IIIb) with lithium aluminium hydride in ether. The stereospecificity was estimated to be 99% retention. A further series of reductions was carried out using complexes of lithium aluminium hydride and terpene alcohols. These reductions proceeded very much faster than the reductions with the alkaloid complexes. In fact, complexes of alkaloids with lithium aluminium hydride appear to be more selective in reductions of methoxysilanes than lithium alkoxyaluminium hydrides.

The results of a series of asymmetric reductions of (±)-mesitylphenylmethylmethoxysilane [(±)-(IVa)] are shown in Table 5. The rate of reduction is significantly lower than with methoxysilanes (IIa) or (IIIa), probably because of the bulk of the mesityl group. The sign of rotation of the silane produced can be related to the configuration at C(9) in the alkaloid, as is the case for the reduction of (IIIa). Again the sign of rotation at 588

TABLE 5

Reductions of (±) mesitylphenylmethylmethoxysilane [(±)-(IVa)] with alkaloid–LiAlH$_4$ complexes

Alkaloids[a]	(1)	(2)	(3)	(4)	(6)
% Redn.[b]	27	34	34	31	15
$[\alpha]_{588}$ Silane	−4·02°	−1·83°	+1·77°	+1·32°	0·00°
$[\alpha]_{588}$ Methoxy-silane	+2·52°	+1·04°	−1·01°	−0·47°	0·00°

[a] See footnote to Table 1. [b] Yields based on the weights of silane isolated.

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[6] H. Lehmkuhl, *Angew. Chem. Internat. Edn.*, 1965, **4**, 600; H. Bock and H. Alt, *J. Amer. Chem. Soc.*, 1970, **92**, 1569.

[7] E. A. Chernyshev and N. G. Tolstikova, *Bull. Acad. Sci., U.S.S.R.*, 1960, 1483; C. Eaborn, 'Organosilicon Compounds,' Butterworth, London, 1958, p. 150.

[8] A. G. Brook, *J. Amer. Chem. Soc.*, 1963, **85**, 3051.

[9] R. A. Barnes and B. R. Juliano, *J. Amer. Chem. Soc.*, 1959, **81**, 6462.

nm of the residual methoxysilane was opposite to that of the silane produced, but this does not necessarily mean that the reduction has proceeded with retention of configuration. On the basis of the suggestion[10] that, for closely related series of optically active carbon compounds containing aromatic groups the sign of the Cotton effect around 260 nm reflects the relative configuration, it must be assumed that methoxysilane (—)-(IVa) and silane (+)-(IVb) possess the same configuration and that the reduction has proceeded with inversion. Further work is clearly desirable on this point.

The absolute configuration of (IVb) cannot be inferred with certainty. The only known optically active carbon compound containing a mesityl and a phenyl group together on an asymmetric centre is *S*(—)-mesitylphenylmethanol.[11] Application of Brewster's analysis of group polarisabilities[12] leads to the conclusion that the mesityl group has a higher polarisability than the phenyl group and this, in turn, leads to the assignment of the *S*-configuration to (—)-(IVb). There appears no reason to doubt the assignment of configuration to (—)-mesitylphenylmethanol, which was made on the basis of an asymmetric synthesis, but it might be considered desirable to have confirmation by an independent method. Moreover, considerations based on group polarisabilities alone may be questionable because of the possibility of important conformational effects due to the bulk of the mesityl group. The assignment of configuration to (—)-(IVb) must, therefore, be regarded as provisional.

In order to compare the steric effects of groups of different size the asymmetric reduction of (±)-phenylisopropylmethylmethoxysilane [(±)-(Va)] was carried out. The results are shown in Table 6. From the Table it can be seen that the extent, and hence rate, of reduction is very similar for (Va) as for (IIa) but that for the former compound the stereoselectivity is, in general, greater. By applying Brewster's rules of conformational asymmetry it can be inferred that (+)-phenylisopropylmethylsilane has the *S*-configuration. A comparison of the o.r.d. curves of (+)-phenylisopropylmethylsilane and (—)-phenylisopropylmethylmethoxysilane indicates that the reduction has proceeded with retention of configuration.

TABLE 6

Reductions of (±) phenylisopropylmethylmethoxysilane [(±)-(Va)] with alkaloid–$LiAlH_4$ complexes

Alkaloid	(1)	(2)	(3)	(4)
% Redn.	57	41	58	27
$[\alpha]_{588}$ Silane	$-0{\cdot}03°$	$+0{\cdot}13°$	$+0{\cdot}30°$	$+0{\cdot}73°$
$[\alpha]_{588}$ Methoxysilane	$+0{\cdot}66°$	$-0{\cdot}57°$	$-4{\cdot}61°$	$0{\cdot}00°$

Stereochemical studies on optically active silanes have hitherto been confined almost exclusively to systems with one or more aromatic groups attached to silicon, because of the lack of simple chiral alkylsilanes. So far the only optically active trialkylsilane reported[13] is one where the alkyl groups are bulky and complex. The successful asymmetric reduction of (±)-cyclohexylmethylethylmethoxysilane [(±)-(VIa)] is therefore a useful advance in the study of asymmetric organosilanes. The complex of (+)-cinchonine with lithium aluminium hydride was chosen as the reducing agent because of the high optical yields previously found using this reagent. Both the silane produced and the unreduced methoxysilane had plain negative o.r.d. curves. If we assume that the sign of these curves is related to the configuration[14] then the reduction must have proceeded with inversion of configuration. It is obviously important that further work should be carried out to check this conclusion. Application of Brewster's rules of conformational asymmetry lead to the silane (—)-(VIb) being assigned the *S*-configuration, and this is supported by the principle of isoconfigurational series since the laevorotatory carbon analogue[15] has the *S*-configuration.

The suggestion has been made[16] that in these reductions rather than the direct reduction of racemic methoxysilane by a chiral reducing complex there might first be alkoxy-exchange followed by reduction of the unequal amounts of diastereoisomers formed or the unequal amount of methoxysilane enantiomers remaining. This seems extremely unlikely both from a consideration of relative rates of reduction and from an examination of reaction mixtures for exchange products. For example complete reduction of 1-naphthylphenylmethyl-(—)-menthoxysilane requires a five-fold excess of lithium aluminium hydride at 80—90° for 18 h, whereas 1-naphthylphenylmethylmethoxysilane is completely reduced in 16 h at room temperature. Furthermore, if appreciable exchange took place the reaction products would show this; examination by n.m.r. spectroscopy and t.l.c. of the reaction mixture from the partial reduction of (±)-(Ia) with a complex of lithium aluminium hydride and (—)-menthol, however, showed no evidence of any menthoxysilane being present. Similar investigations likewise failed to reveal the presence of any exchange products from the reduction of the methoxysilane (IIa) by the same reducing complex.

A complete rationalisation of the results and the steric interactions controlling the course of the reactions is not possible at this stage. Attention has already been drawn to the patterns present in some of the sets of reactions, but experience suggests[17] that it would be unwise to carry speculation and reasoning by analogy too far. The work is being extended to other systems where it is hoped that interpretation of steric effects will be easier.

A comprehensive study of the o.r.d. and c.d. spectra of

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[10] P. Crabbe, in ' Topics in Stereochemistry,' eds. N. L. Allinger and E. E. Eliel, Interscience, New York, 1967, vol. 1, p. 109.

[11] O. Cervinka, V. Suchan, and B. Masar, *Coll. Czech. Chem. Comm.*, 1965, **30**, 1693.

[12] J. H. Brewster, *J. Amer. Chem. Soc.*, 1959, **81**, 5475.

[13] G. R. Buell, L. Spialter, and J. D. Austin, *J. Organometallic Chem.*, 1968, **14**, 309.

[14] Ref. 1, p. 309.

[15] D. J. Cram and J. Tadanier, *J. Amer. Chem. Soc.*, 1959, **81**, 2737.

[16] G. J. D. Peddle, personal communication.

[17] K. Mislow, M. G. Green, P. Laur, J. T. Melillo, T. Simmons, and A. L. Ternay, *J. Amer. Chem. Soc.*, 1965, **87**, 1958; A. G. Brook and J. D. Pascoe, *ibid.*, 1871, **93**, 6224.

1-naphthylphenylmethylsilane and its derivatives [18] has been published. Our results are in essential agreement with this work, but better u.v. penetration enabled us to detect some additional detail of the c.d. spectrum of (Ib) in the 340—270 nm region. Compounds (IIIa) and (IIIb) give plain o.r.d. curves over the range 588—294 nm, whilst the c.d. spectra show a number of maxima in the range 275—205 nm. The o.r.d. curves of (+)-(IVa) and (—)-(IVb) are of interest. The former gives a plain curve over the range 500—600 nm, whereas the latter gives a curve which becomes increasingly laevorotatory from 588—380 nm, passes through a broad trough, and then becomes dextrorotatory until the cut off at 294 nm (Figure 1). C.d. measurements show the presence of a weak positive peak for both compounds at 281 nm. If the rule quoted above [12] is used to assign relative configurations to (+)-(IVa) and (—)-(IVb) then the reduction must proceed with inversion of configuration. It must be stressed however that this rule has been formulated on the basis of results obtained for carbon compounds and it may not necessarily be applicable to silicon compounds, particularly in view of the interactions between silicon atoms and aromatic groups as shown [19] by a study of u.v. spectra. Compounds (IIa), (IIb), (Va), and (Vb) all gave plain dispersion curves in the range 588—300 nm. Below 300 nm absorption was too great to permit further o.r.d. or c.d. measurements. Both (—)-(VIa) and (—)-(VIb) showed plain dispersion curves in the range 558—300 nm, which suggests that this reduction also may have proceeded with inversion of configuration.

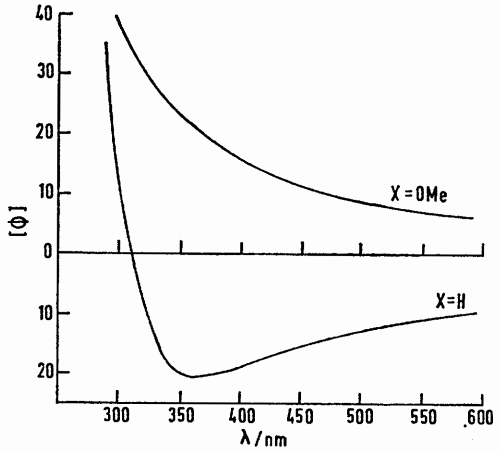

FIGURE 1 O.r.d. curves for MesPhMeSiX: Mes = 2,4,6-trimethylphenyl

There are many known examples of the magnetic nonequivalence of protons in diastereoisomers and of the consequent use of n.m.r. spectroscopy in analysing mixtures of such diastereoisomers.[20] The technique has also been applied to organosilicon compounds,[21] and we have already reported [22] on its use in analysing mixtures of (—)-1-naphthylphenylmethyl-(—)-menthoxysilane (VII) and (+)-1-naphthylphenylmethyl-(—)-menthoxysilane (VIII). In the 60 MHz spectrum of this mixture there are four sharp resonances with an intensity of three protons centred at τ 9·50 which are found to be two superimposed doublets whose chemical shift depends on the chirality at the silicon atom.

The high-field doublets were originally thought to be due to the methyl group on C(5) of the menthoxy-residue, but a rigorous analysis [23] of the spectra of diastereoisomeric phosphinate menthyl esters shows that similar high-field doublets are caused by the *pro-S*-methyl group of the isopropyl residue. In view of the general similarity of the spectra and the similar coupling constants for the doublets in the two series it now seems likely that the high-field resonances in the silicon compounds are also due to the *pro-S*-methyl group.

The relative intensities of these doublets may be used to assess diastereoisomeric composition of mixtures. Additional information can be obtained from a consideration of differences in resonances in the τ 9·0—9·2 region, although these are too close to the resonances of the methyl on silicon to be of great value on their own. At 100 MHz the high-field doublets at τ 9·4—9·6 are separated to the extent that two of the peaks overlap and the region has the appearance of an unsymmetrical triplet. The region at τ 9·0—9·3 gives similar indications to the 60 MHz spectra but the separation is still insufficient for qualitative purposes. At 220 MHz there is sufficient resolution to allow assignment of the other methyl doublets of the menthoxy-group and the methyl on silicon. The positions of these protons, deduced by analogy with the results for the menthyl phosphinate esters, together with the results of a variable-temperature study are given in Table 7.

TABLE 7

Temperature dependence of the n.m.r. spectra of (VII) and (VIII) (solvent CCl_4)

	21°	0°	−20°	−40°	
(VII)	9·55(0)	9·56(8)	9·59(0)	9·60(0)	H_a
(VIII)	9·48(8)	9·50(1)	9·52(0)	9·53(2)	
(VII)	9·25(0)	9·25(0)	9·25(5)	9·25(0)	H_b
(VIII)	9·23(1)	9·23(4)	9·23(8)	9·23(7)	
(VII)	9·18(6)	9·18(4)	9·18(5)	9·17(5)	H_c
(VIII)	9·23(5)	9·23(6)	9·24(2)	9·23(5)	
(VII)	9·18(6)	9·18(4)	9·18(5)	9·17(5)	H_d
(VIII)	9·10(0)	9·09(8)	9·09(4)	9·08(8)	

τ Values calculated from Me_4Si internal standard on expanded 220 MHz spectra. The values are reported to three places of decimals but the figures in parentheses are not so reliable. J_{HCH} of H_a and H_d are 7·0 Hz and of H_c 6·0 Hz.

The coupling constants for the doublets H_a and H_d (see

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[18] L. H. Sommer and J. McLick, *J. Amer. Chem. Soc.*, 1969, **91**, 2001.

[19] H. Alt, H. Bock, F. Gerson, and J. Heinzer, *Angew. Chem. Internat. Edn.*, 1967, **6**, 941.

[20] M. Raban and K. Mislow, in ' Topics in Stereochemistry,' eds. N. L. Allinger and E. E. Eliel, Interscience, New York, 1967, vol. 2, p. 199, and references therein.

[21] J. F. Klebe and H. Finkbeiner, *J. Amer. Chem. Soc.*, 1968, **90**, 7255; A. G. Brook, C. M. Warner, and W. W. Linburg, *Canad. J. Chem.*, 1967, **45**, 1231.

[22] A. Holt, A. W. P. Jarvie, and G. J. Jervis, *J. Organometallic Chem.*, 1970, **21**, 75.

[23] R. A. Lewis, O. Korpium, and K. Mislow, *J. Amer. Chem. Soc.*, 1968, **90**, 4847.

Figure 2) are 7·0 and that for H_c is 6·0 Hz, compared with respective values of 7·0 and 4·5—5·5 in the phosphinate esters. The upfield shift of the H_a doublet in diastereoisomers (VII) and (VIII) is attributable to the anisotropy of the aromatic groups rather than to any effect of the silicon atom. No such shift is observed in the spectrum of a mixture of diastereoisomeric cyclohexylethylmethylmenthoxysilanes. This upfield shift seems to be general for menthoxy-derivatives of any silane possessing an aromatic group, as may be seen from the results shown in Table 8. Examination of these resonances might provide a general method for determining the optical purity of chiral organosilanes possessing an aromatic group provided that there is available a stereospecific synthesis of the menthoxy-derivative. Unfortunately extensive racemisation was found to occur during a preliminary attempt to react (IIIb) and (—)-menthol using a palladium on charcoal catalyst. Moreover it appears that if a stereospecific synthesis of the (—)-menthoxy-derivative could be found the absolute configuration at the silicon atom might be inferred from the n.m.r. spectrum. A number of cases are already known [24] where the position of diastereotopic resonances may be used for correlation of configuration. Closely analogous to the compounds described in this paper are the (—)-menthyl phosphinates and sulphinates where it has been shown [23] that the diastereoisomer with the higher field doublet is the one with the *S*-configuration at the phosphorus or sulphur atom. Similarly the menthoxysilane (VII) has the *S*-configuration at silicon and the H_a doublet is at higher field than in (VIII). The results of variable-temperature n.m.r. studies (Table 7) show that the resonances of protons H_a in diastereoisomers (VII) and (VIII) move to higher field as the temperature is lowered, whilst the resonances due to H_c and H_d are relatively unaffected. This shows that the magnetic non-equivalence of the H_a and H_d protons is primarily due to conformational preferences, which might be expected to change appreciably with temperature, rather than to intrinsic diastereotopism.[25] This temperature effect is unlikely to be due to changes in solvent–solute interactions, since changes in solvent polarity only slightly effect the chemical shift of H_a. In carbon tetrachloride, carbon disulphide, and dimethyl sulphoxide, these resonances are centred at τ 9·55, 9·52, and 9·50, respectively.

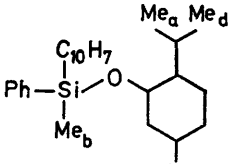

FIGURE 2 Labelling of protons in 1-naphthylphenylmethyl-(—)-menthoxysilanes (VII) and (VIII)

TABLE 8

Proton magnetic resonance spectra of diastereoisomeric menthoxysilanes, $R^1R^2R^3Si$-(—)-menthoxy

R^1	R^2	R^3	Chirality at Si,	High field doublets [a] (τ)
1-Np	Ph	Me	*S*	9·55
1-Np	Ph	Me	*R*	9·49
$PhCH_2$	Ph	Me		9·40
$PhCH_2$	Ph	Me		9·45
Et	Ph	Me		9·37
Et	Ph	Me		9·43
Et	cyclo-C_6H_{11}	Me		9·27 [b]
Et	cyclo-C_6H_{11}	Me		9·27 [b]

[a] J_{HCH} = 7 Hz. [b] Methyl doublet in pure (—)-menthol is observed [23] at τ 9·18. 1-Np = 1-naphthyl.

The results of a variable-temperature study of the n.m.r. spectrum of the mixture of diastereoisomeric (±)-phenylethylmethyl-(—)-menthoxysilanes are shown in Table 9. The increase in Δν as the temperature is lowered once again points [25] to conformational preference as the principle reason for the magnetic non-equivalence of protons H_a and H_d.

TABLE 9

Temperature dependence of the n.m.r. spectra of (±)-phenylethylmethyl-(—)-menthoxysilane diastereoisomers

Temp.	Diastereotopic resonances τ		Δν Hz
20°	9·35(6)	9·42(2)	14·5
0	9·39(7)	9·48(4)	14·8
—20	9·40(3)	9·47(3)	15·5
—40	9·42(7)	9·50(0)	16·0

Solvent CCl_4.

These n.m.r. studies were extended to investigate the composition of some diastereoisomeric alkoxysilane mixtures formed both by equilibration procedures and by reactions under kinetic control. Reactions of (±)-(Ib) with (±)-menthol with a palladium on charcoal catalyst [22,26] gave a mixture which analysed as 55% of (VII) and 45% of (VIII), together with the same proportions of the mirror-image compounds. Since this reaction has been shown to be stereospecific [26] the product composition must result from kinetic control. The same diastereoisomers are formed preferentially by methods involving equilibration of configuration at the silicon atom. By similar studies (±)-1-naphthylphenylmethyl-(±)-1-phenylethoxysilane was found to predominate over (∓)-1-naphthylphenylmethyl-(±)-1-phenylethoxysilane both in kinetically controlled reaction mixtures and in equilibrated mixtures. A number of other alkoxysilanes were prepared from (±)-(Ib) and various optically active alcohols using a palladium on charcoal catalyst. The n.m.r. spectra of both the (—)-bornyloxy and the (—)-isobornyloxysilanes showed evidence of diastereotopic resonances, as also did the reaction mixture from (±)-(Ib) and (±)-methylisopropylmethanol. A separation

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[24] M. Mikolajczyk, M. Para, A. Ejchart, and J. Jurczak, *Chem. Comm.*, 1970, 654; W. H. Pirkle, R. L. Muntz, and I. C. Paul, *J. Amer. Chem. Soc.*, 1971, **93**, 2817.

[25] H. S. Gutowsky, *J. Chem. Phys.*, 1962, **37**, 2196; M. Raban, *Tetrahedron Letters*, 1966, 3105.

[26] L. H. Sommer and J. E. Lyons, *J. Amer. Chem. Soc.*, 1969, **91**, 7061.

of these various diastereoisomers and a fuller analysis of their spectra has so far not been achieved.

EXPERIMENTAL

60 MHz Proton resonance spectra were obtained either on a Perkin-Elmer R10 spectrometer operating at 35° or a Varian Associates A60 instrument. 100 MHz Spectra were obtained on a Perkin-Elmer R14 and 220 MHz spectra on a Varian Associates HA220 instrument. Tetramethylsilane was used as an internal reference throughout. I.r. spectra were obtained on a Perkin-Elmer Infracord 237 and u.v. spectra on a Perkin-Elmer 137. O.r.d. spectra were measured on a Bellingham and Stanley Polarmatic 62 spectropolarimeter and c.d. spectra were measured on a Roussel–Jouan dichrograph. G.l.c. analyses were carried out on a Pye series 104 chromatograph with a katharometer detector and helium as carrier gas. The light petroleum used had b.p. 60—80°, unless otherwise stated.

Preparation of Racemic Methoxysilanes and Silanes.—The methoxysilanes listed below were prepared by the action of the appropriate Grignard reagent on phenylmethyldimethoxysilane in solution in ether.

(±)-1-*Naphthylphenylmethylmethoxysilane* [(±)-(Ia)]. After recrystallisation from hexane this compound had m.p. 57° and i.r. and n.m.r. spectra as quoted in the literature.

(±)-*Phenylethylmethylmethoxysilane* [(±)-(IIa)]. Examination by g.l.c. (9 ft × $\frac{1}{8}$ in o.d. stainless-steel tube, S.E. 30 packing on firebrick, carrier gas helium at 50 ml min^{-1}, 115°) showed that this compound contained 12% phenylmethyldimethoxysilane. It was used without further purification.

(±)-*Benzylphenylmethylmethoxysilane* [(±)-(IIIa)]. This compound was obtained as a clear colourless oil, b.p. 90—91°/0·05 mmHg, τ (100 MHz; CCl_4) 9·74 (3H, s), 7·65 (2H, ABq, *J* 1·48), 6·65 (3H, s), and 2·4—3·1 (10H, m) (Found: C, 74·4; H, 7·6; Si, 11·8. $C_{15}H_{18}OSi$ requires C, 74·3; H, 7·5; Si, 11·6%).

(±)-*Mesitylphenylmethylmethoxysilane* [(±)-(IVa)]. This compound was obtained as a colourless oil, b.p. 134°/0·6 mmHg, τ (60 MHz; CCl_4) 9·35 (3H, s), 7·80 (3H, s), 7·70 (6H, s), 6·63 (3H, s), 3·26 (2H, s), and 2·70 (5H, m) (Found: C, 75·4; H, 8·2; Si, 10·5. $C_{17}H_{22}OSi$ requires C, 75·5; H, 8·2; Si, 10·4%).

(±)-*Phenylisopropylmethylmethoxysilane* [(±)-(Va)]. After work-up this compound was distilled under reduced pressure and finally purified by chromatography on silica gel using benzene as eluant, to give the product as a colourless oil.

The silanes, where required, were prepared by heating under reflux a solution of the methoxysilane in diethyl ether with lithium aluminium hydride for periods of time between 15 and 24 h, as necessary.

(±)-*Benzylphenylmethylsilane* [(±)-(IIIb)]. This compound was obtained as a colourless oil, τ (100 MHz; CCl_4) 9·73 (3H, d, *J* 3·7 Hz), 7·65 (2H, m), 5·50 (1H, sextet), and 2·4— 3·1 (10H, m); $\nu_{max.}$ (thin film) 2120s (Si–H).

(±)-*Mesitylphenylmethylsilane* [(±)-(IVb)]. This compound was obtained as a colourless oil, τ (60 MHz; CCl_4) 9·39 (3H, d, *J* 4·0 Hz), 7·80 (3H, s), 7·69 (6H, s), 4·75 (1H, q, *J* 4·0 Hz), 3·27 (2H, s), and 2·90—2·45 (5H, m); $\nu_{max.}$ (thin film) 2140s (Si–H).

(±)-*Phenylisopropylmethylsilane* [(±)-(Vb)]. After work-up this compound was purified by chromatography on silica gel using a 1 : 4 mixture of benzene and light petroleum as eluant, to give a colourless oil, τ (60 MHz; CCl_4) 9·76 (3H, d, *J* 4·0 Hz), 9·4—8·7 (7H, m), and 5·83 (1H, m); $\nu_{max.}$ (thin film) 2105s (Si–H).

Reduction of (±)-1-*Naphthylphenylmethylmethoxysilane with Complexes of Lithium Aluminium Hydride and Alkaloids.*—The following alkaloids were used: (+)-quinidine, recrystallised from absolute ethanol, dried at 120° to give anhydrous material $[\alpha]_{588}$ +243° (*c* 0·044, ethanol); (−)-quinine, dried at 120° overnight $[\alpha]_{588}$ −145°; (+)-cinchonine, dried at 120° overnight $[\alpha]_{588}$ +204° (*c* 0·41, ethanol); (−)-cinchonidine, dried at 120° overnight $[\alpha]_{588}$ −104·3°; (+)-ψ-ephedrine, distilled *in vacuo*, b.p. 132°/18 mmHg, $[\alpha]_{588}$ +49·4° (ethanol), m.p. 117°; (−)-ephedrine, distilled *in vacuo*, b.p. 129°/4 mmHg, $[\alpha]_{588}$ −4·96°.

A typical reduction was carried out as follows. The complex hydride was prepared *in situ* by the addition of (+)-quinidine (3·56 g, 11 mmol) to a solution of lithium aluminium hydride (0·42 g, 11 mmol) in diethyl ether (100 ml, freshly distilled from lithium aluminium hydride). The solution was refluxed for 30 min and a solution of (±)-(Ia) (10 g, 34·8 mmol) in ether (20 ml) was added to it. After refluxing for a further 4 h the excess of hydride was decomposed with cold dilute sulphuric acid, the ether layer was washed several times with water, and dried (Na_2SO_4). Removal of the ether left an oil (9·07 g). This product (8·8 g) was chromatographed on a column of silica gel. Elution with a mixture of benzene–light petroleum (1 : 9) gave 1-naphthylphenylmethylsilane (Ib) (2·93 g). Further elution, with benzene, gave (Ia) (4·3 g). The n.m.r. and i.r. spectra of these products were identical with those of authentic racemic samples, and their u.v. extinction coefficients and mobilities on t.l.c. agreed very closely with those of authentic samples.

The crystals of (Ib) were pressed between filter papers to remove a small quantity of oily material and then recrystallised three times from hexane (spectroscopic grade) to give pure (+)-(Ib), m.p. 63° $[\alpha]_{588}$ +35·5° (*c* 0·12 hexane) (lit.[27] m.p. 64°, $[\alpha]_D$ +35·0°). The optical purity of (Ia) could not be increased by similar recrystallisation so it was completely reduced with lithium aluminium hydride in diethyl ether. Recrystallisation of the product gave (−)-(Ib), m.p. 59°, $[\alpha]_{588}$ −29° (*c* 0·34, hexane).

The other reductions in this series were carried out in the manner described above, using one fifth of the above quantities. In each case the extent of reduction was calculated on the amount of silane isolated. The purity of the products was checked by t.l.c. and i.r. spectroscopy and optical rotations were measured at various wavelengths.

The characteristics of the products obtained using other alkaloids were as follows: with (−)-quinine, (Ib) 0·63 g (35·4%) and (Ia) 0·60 g; with (+)-cinchonine, (Ib) 0·76 g (42·7%) and (Ia) 1·17 g; with (−)-cinchonidine, (Ib) 0·50 g (28%) and (Ia) 1·12 g; with (−)-ephedrine, (Ib) 0·40 g (22·5%) and (Ia) 1·28 g; with (+)-ψ-ephedrine, (Ib) 0·49 g (27·5%) and (Ia) 0·95 g.

Reduction of (+)-(Ia) *with Complexes of Lithium Aluminium Hydride and Alcohols.*—The following alcohols [28] were used: (−)-menthol, distilled, b.p. 119°/30 mmHg $[\alpha]_{588}$ −32·6° (*c* 4·07, ethanol {lit., b.p. 111°/20 mmHg, $[\alpha]_D$ −50·1° (ethanol)}; (−)-borneol, distilled, b.p. 212°, m.p. 212—213° (sealed tube), $[\alpha]_{588}$ −22° (ethanol) {lit., b.p. 212°, m.p. 208° $[\alpha]_D$ −37·74°}; (−)-isoborneol, prepared by reduction of (+)-camphor with lithium aluminium hydride, $[\alpha]_{588}$ −14·2° (methanol) {lit.

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[27] L. H. Sommer, C. L. Frye, G. A. Parker, and K. W. Michael, *J. Amer. Chem. Soc.*, 1964, **86**, 3271.

[28] ' Dictionary of Organic Compounds ', eds. J. R. A. Pollock and R. Stevens, Eyre and Spottiswoode, London, 1965.

$[\alpha]_{\rm D}$ −32·3° (methanol)}; cholesterol, $[\alpha]_{588}$ −36·7° (*c* 1·87, chloroform) {lit., $[\alpha]_{\rm D}$ −31·12° (ether)}; (+)-α-fenchol $[\alpha]_{\rm D}$ +10·4° (*c* 4·67, ethanol) {lit., $[\alpha]_{\rm D}$ +10·36°}; lanosterol, m.p. 130—131°, $[\alpha]_{588}$ +41·2° (*c* 0·85, chloroform) {lit., m.p. 140—141°, $[\alpha]_{\rm D}$ +58° (chloroform)}; (+)-octan-2-ol $[\alpha]_{588}$ +7·8° (*c* 13, methanol) {lit., $[\alpha]_{\rm D}$ +9·9°}.

A typical reduction was carried out as follows. A solution of (±)-(Ia) (2 g, 6·96 mmol), lithium aluminium hydride (0·085 g, 2·24 mmol), and (−)-menthol (0·349 g, 2·24 mmol) in ether (24 ml) was heated under reflux for 4 h. The mixture was worked-up as before to give a product (2·12 g) which still contained menthol. This was chromatographed on silica gel, as before to give (Ib) (0·879 g). The n.m.r. and i.r. spectra of these products were identical with those of authentic racemic samples. No trace was found of the presence of (−)-1-naphthylphenylmethyl-(−)-menthoxysilane or (+)-1-naphthylphenylmethyl-(−)-menthoxysilane.

Further reductions were carried out in the same manner. The characteristics of the products obtained using other alcohols were as follows: with (−)-borneol, (Ib) 1·0 g (56·2%) and (Ia) 0·32 g; with (−)-isoborneol, (Ib) 0·83 g (46·6%) and (Ia) 0·95 g; with (+)-α-fenchol, (Ib) 0·56 g (31·5%) and (Ia) 0·84 g; with cholesterol, (Ib) 0·55 g (31·0%); with lanosterol, no reduction occurred and only (Ia) was recovered; with (+)-octan-2-ol, (Ib) 0·42 g (23·6%) and (Ia) 1·05 g.

The reduction with lanosterol was repeated following the same procedure, except that the reaction mixture was refluxed for 24 h to give (Ib) 0·10 g (5·6%) no observable optical activity, (Ia) no observable optical activity.

Reductions of (±)-(IIa) *with Complexes of Lithium Aluminium Hydride and Alkaloids.*—A typical reduction was carried out as follows. Lithium aluminium hydride (0·207 g, 5·42 mmol), (+)-cinchonine (1·63 g, 5·55 mmol), and (±)-(IIa) (1·495 g, 8·27 mmol) in ether (60 ml) was heated under reflux for 24 h. The mixture was worked-up as before except that saturated aqueous ammonium chloride was used to decompose the excess of lithium aluminium hydride. The product was an oil (1·54 g). Examination by g.l.c. showed the presence of phenylethylmethylsilane (IIb) (56%), (IIa) (43%), and a small proportion of phenylmethylsilane. The mixture was worked-up by column chromatography on silica gel. Elution with a 1 : 4 mixture of benzene and light petroleum gave (IIb) (0·57 g, 46%). Further elution, with benzene, gave (IIa) (0·216 g, 14·5%). The i.r. and n.m.r. spectra of these products were identical with those of authentic racemic samples.

The characteristics of the products obtained using other alkaloids were as follows: with (−)-cinchonidine, (IIb) 0·57 g (46%; by g.l.c. 51%) and (IIa) 0·31 g (21%); with (+)-quinidine, (IIb) 0·59 g (47%; by g.l.c. 54%) and (IIa) 0·48 g (32%); with (−)-quinine, (IIb) 0·65 g (52%; by g.l.c. 64%) and (IIa) 0·25 g (17%); with (+)-ψ-ephedrine, (IIb) 0·20 g (16%; by g.l.c. 34%); and (IIa) 0·60 g (40%).

Reduction of (±)-(IIa) *with a Complex of Lithium Aluminium Hydride and* (−)-*Menthol.*—A solution of (±)-(IIa) (1·5 g, 8·27 mmol) and a 1 : 1 complex (5·51 mmol) of lithium aluminium hydride and (−)-menthol in ether (40 ml) was heated under reflux for 4 h to give a 65% yield of (IIb). The mixture was worked-up as before to give (IIb) $[\alpha]_{588}$ −0·03° (optical yield 1%) and (IIa) $[\alpha]_{588}$ +0·11°.

Reduction of (±)-(IIIa) *with a Complex of Lithium Aluminium Hydride and* (+)-*Cinchonine.*—A solution of (±)-(IIIa) (2·0 g, 8·25 mmol), lithium aluminium hydride (0·207 g, 5·42 mmol), and (+)-cinchonine (1·63 g, 5·54 mmol) in diethyl ether (60 ml) was heated under reflux for 24 h. Work-up as before gave an oil (1·96 g) which was chromatographed on a silica-gel column. Elution with a mixture of benzene–light petroleum (1 : 9) gave (IIIb) (0·711 g, 41%); the n.m.r. spectrum was identical with that of a racemic sample. Further elution, with benzene, gave (IIIa) (0·76 g, 38%).

The characteristics of the products obtained using other alkaloids were as follows: with (−)-cinchonidine, (IIIb) 0·843 g (48%) and (IIIa) 0·873 g; with (+)-quinidine, (IIIb) 0·52 g (28·5%) and (IIIa) 1·09 g (54·5%); with (−)-quinine, (IIIb) 0·66 g (37%) and (IIIa) 0·73 g (36·5%); with (+)-ψ-ephedrine, (IIIb) 0·35 g (20%) and (IIIa) 1·43 g (71·5%); with (−)-ephedrine, (IIIb) 0·12 g (6·8%) and (IIIa) 1·56 g (78%).

Reductions of (±)-(IIIa) *with Complexes of Lithium Aluminium Hydride and Alcohols.*—The procedure was similar to that previously described, the reaction mixtures being refluxed for 4 h. The characteristics of the products were as follows: with (−)-menthol, (IIIb) 1·04 g (60%; $[\alpha]_{588}$ +0·18°) and (IIIa) 0·33 g (17%; $[\alpha]_{588}$ −0·45°); with (−)-borneol, (IIIb) 1·38 g (79%; no observable optical activity) and (IIIa) 0·20 g (10%; no observable optical activity); with (+)-fenchol, (IIIb) 1·03 g (59%; no observable optical activity) and (IIIa) 0·28 g (14%; no observable optical activity).

Reduction of (+)-(IIIa) *to* (+)-(IIIb) *with Lithium Aluminium Hydride.*—A suspension of lithium aluminium hydride (0·5 g) in diethyl ether containing (+)-(IIIa) ($[\alpha]_{588}$ +1·86°; 0·633 g) was stirred under reflux for 5 h. Work-up and chromatography on a silica-gel column gave (+)-(IIIb) (0·52 g; $[\alpha]_{588}$ +6·45°).

Reduction of (±)-(IVa) *with Complexes of Lithium Aluminium Hydride and Alkaloids.*—The method of reduction and work-up of products were the same as described for (IIIa). The characteristics of the products obtained with the various alkaloids were as follows: with (+)-quinidine, (IVb) 0·609 g (34%) and (IVa) 1·0 g; with (−)-quinine, (IVb) 0·48 g (27%) and (IVa) 0·80 g; with (+)-cinchonine, (IVb) 0·554 g (31%) and (IVa) 1·013 g; with (−)-cinchonidine (IVb) 0·61 g (34%) and (IVa) 1·0 g; with (+)-ψ-ephedrine the reaction mixture was refluxed for 48 h to give (IVb) 0·262 g (15%; no observable optical activity) and (IVa) 0·99 g (no observable optical activity).

Reductions of (±)-(Va) *with Complexes of Lithium Aluminium Hydride and Alkaloids.*—The methoxysilane (1·62 g, 8·35 mmol) was reduced and the mixture worked-up by the procedure described for the reduction of (±)-(IIa). The characteristics of the products obtained with the various alkaloids were as follows: with (+)-cinchonine, (Vb) 0·35 g (25·5%; by i.r. 27%), (Va) 0·51 g (n.m.r. spectroscopy indicated the presence of 20% disiloxane in this fraction. Racemisation and condensation had probably occurred during work up); with (−)-cinchonidine (1·43 g of methoxysilane were used) was obtained (Vb) 0·34 g (28·0%; by g.l.c. 41·0%) and (Va) (0·89 g); with (+)-quinidine, (Vb) 0·55 g (40·2%) and (Va) 0·34 g; with (−)-quinine (Vb) 0·48 g (35%) and (Va) 0·28 g.

Preparation of Cyclohexylmethyldichlorosilane.—This compound, b.p. 74—76°/12 mmHg (lit.,[29] b.p. 201—202°/760 mmHg) was prepared by the method described in the literature.

Preparation of (±)-*Cyclohexylethylmethylchlorosilane.*—

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[29] J. L. Speier, J. A. Webster, and G. H. Barnes, *J. Amer. Chem. Soc.*, 1957, **79**, 974.

Ethylmagnesium bromide and cyclohexylmethyldichlorosilane in diethyl ether were heated under reflux for two days under nitrogen. Work-up gave the product, b.p. 80°/9 mmHg. Examination by g.l.c. showed it to contain cyclohexylmethyldichlorosilane (20%) and cyclohexyldiethylmethyl silane (7%).

Preparation of (±)-*Cyclohexylethylmethylmethoxysilane* [(±)-(VIa)].—(±)-Cyclohexylethylmethylchlorosilane (5 g, 26·3 mmol) was treated with anhydrous methanol (3 ml) and triethylamine (5 ml) in light petroleum (15 ml). After filtration the solvent was removed to leave the product (4.23 g). Examination by g.l.c. showed it to contain cyclohexylmethyldimethoxysilane (17%) and cyclohexyldiethylmethylsilane (13%).

Reduction of (±)-(VIa) *with a Complex of Lithium Aluminium Hydride and* (+)-*Cinchonine*.—(+)-Cinchonine (1·37 g, 4·66 mmol), lithium aluminium hydride (0·177 g, 4·66 mmol), and (±)-(VIa) (0·93 g, 3·8 mmol of above product without further purification) in diethyl ether (60 ml) was heated under reflux for 7 days. The mixture was worked-up by treatment with ammonium chloride solution as above to give a product (1·04 g) with a strong i.r. absorption at 2095 cm^{-1} (Si–H), which was chromatographed on silica gel. Elution with benzene–light petroleum (1 : 9) gave the silane (VIb) (0·19 g). Examination by g.l.c. showed it to contain cyclohexyldiethylmethylsilane (30%). I.r. (thin film) showed $\nu_{\text{max.}}$ 2100s cm^{-1} (Si–H), absorptions for silanol, disiloxane, or methoxysilane were absent. O.r.d. gave $[\alpha]_{588}$ −0·11°, $[\alpha]_{400}$ −0·30°, $[\alpha]_{303}$ −0·76°, and $[\alpha]_{286}$ −96°. Further elution, with benzene, gave (VIa) (0·18 g), shown by g.l.c. examination to contain cyclohexyldiethylmethylsilane (14%). Its i.r. spectrum was identical with that of a racemic sample. O.r.d. gave $[\alpha]_{588}$ −0·58°, $[\alpha]_{400}$ −1·07°, and $[\alpha]_{312}$ −1·82°. Owing to the high volatility of (VIa) and (VIb) it was difficult completely to remove solvents after chromatography and the residual benzene reduced u.v. penetration during o.r.d. measurements. Subsequent experiments showed that (VIb) could be eluted from a silica-gel column with a 1 : 4 mixture of dichloromethane and light petroleum (b.p. 30—40°); (IVa) was eluted by pure dichloromethane followed by ether.

Preparation of Diastereosiomeric 1-*Naphthylphenylmethylalkoxysilanes*.—By reaction of (±)-1-naphthylphenylmethylsilane with the appropriate alcohol, as previously described,[22] diastereoisomeric alkoxysilanes were prepared, in yields dependent on the alcohol used, from (±)-menthol (78%), (±)-1-phenylethanol (68%), (±)-methylisopropylmethanol (47%), (−)-borneol (47%), and (−)-isoborneol (22%). With the last two alcohols the preparation was performed using an excess of (±)silane in order to detect preferential diastereoisomer formation. The yields (in parentheses) are calculated on the alcohol taken. The purity of the products was established by t.l.c. using 7% (v/v) benzene in light petroleum, and by spectroscopic studies.

Preparation of (±)-*Phenylethylmethyl*-(−)-*menthoxysilane*.—A solution of (±)-(IIa) (10 g, 0·06 mol) and (−)-menthol (8·5 g, 0·06 mol) in dry toluene (20 ml) was heated under reflux for 2 h with powdered potassium hydroxide (0·01 g). The azeotropic mixture of methanol and toluene was slowly distilled off. The solution remaining was washed with water and dried (Na_2SO_4).

Equilibration of (±)-1-*Naphthylphenylmethyl*-1-*phenylethoxysilane with Potassium Hydroxide in Toluene*.—(±)-1-Naphthylphenylmethyl-1-phenylethoxysilane (0·846 g) (diastereoisomeric ratio 56 : 44) and (±)-1-phenylethanol (1·0 ml) were heated at 84° for 5 h with powdered potassium hydroxide (0·006 g) in dry toluene (50 ml) with constant stirring. After purification by chromatography on silica gel the product (0·800 g, 95%) had a diastereoisomeric ratio of 60 : 40. Further treatment under the above conditions did not alter this ratio. The major diastereoisomer possessed a resonance for methyl on silicon at τ 9·34 and the other diastereoisomer gave a resonance at τ 9·39.

The authors thank Midland Silicones Ltd. for the gift of chemicals, Professor W. Klyne and Dr. P. M. Scopes for c.d. spectra, and the S.R.C. for a grant (to G. J. J.) and for 220 MHz n.m.r. spectra. Mr. B. Ashworth assisted with some of the work on the reduction of (±)-cyclohexylethylmethylmethoxysilane.

[2/1184 *Received*, 23*rd May*, 1972]