83. *Organosilicon Compounds. Part XXX.*[1] *The Stereochemistry of the Cleavage of a Silicon–Aryl Bond by Bromine.*

By C. EABORN and O. W. STEWARD.

Optically active *p*-methoxyphenylmethyl-1-naphthylphenylsilane has been prepared from the reaction in ether between *p*-methoxyphenyl-lithium and optically active methyl-1-naphthylphenylsilyl hydride, chloride, or menthoxide. The coupling seems to involve inversion of configuration when the chloride is used and retention when the hydride is used.

Cleavage of the *p*-methoxyphenyl-silicon bond by bromine in benzene or carbon tetrachloride appears to proceed with inversion of configuration. This is taken to rule out a four-centre mechanism for the cleavage, and other possibilities are discussed.

The cleavage mentioned is accompanied by some bromine cleavage of silicon–naphthyl bonds and also by some hydrogen bromide cleavage; these cleavages probably also involve predominant inversion of configuration at the silicon atom.

THE work of Sommer and Frye and their colleagues has made available optically active methyl-1-naphthylphenylsilicon compounds, R_3SiX, and has established the stereochemical course of many of their reactions.[2-4] To throw light on the mechanism of cleavage of aryl–silicon bonds by electrophilic reagents, we have prepared optically active *p*-methoxyphenylmethyl-1-naphthylphenylsilane, $R_3Si{\cdot}C_6H_4{\cdot}OMe$-*p*, and have studied the stereochemistry of the cleavage of the Si–$C_6H_4{\cdot}OMe$ bond by bromine in benzene and carbon tetrachloride. We find a high degree of retention of optical activity, but there appears to be inversion of configuration at the silicon atom.

We prepared optically active *p*-methoxyphenylmethyl-1-naphthylphenylsilane by use of *p*-methoxyphenyl-lithium in ether from three optically active R_3SiX compounds. From the more lævorotatory diastereoisomer of $R_3Si{\cdot}O{\cdot}$Menthyl-(—), $[\alpha]_D^{21}$ —54·8 (*c* 12·7 in cyclohexane), the (—)-$R_3Si{\cdot}C_6H_4{\cdot}OMe$-*p* compound, $[\alpha]_D^{20}$ —6·17 (*c* 7·7 in benzene), was obtained in 91% yield. From the (+)-silicon hydride, (+)-R_3SiH, $[\alpha]_D^{21}$ +33·0 (*c* 8·3 in cyclohexane), the (—)-$R_3Si{\cdot}C_6H_4{\cdot}OMe$-*p* compound, $[\alpha]_D^{19}$ —6·0 (*c* 7·7 in benzene), was obtained in 77% yield. From the (—)-R_3SiCl compound [formed from the (+)-R_3SiH compound, $[\alpha]_D^{21}$ +33·0 (*c* 8·3 in cyclohexane), and chlorine but not isolated] the (+)-$R_3Si{\cdot}C_6H_4{\cdot}OMe$-*p* compound $[\alpha]_D^{19}$ +5·72° (*c* 7·8 in benzene) was obtained in 98% yield. The melting points of the products were in the range 70—73°, while that of the racemic material, (±)-$R_3Si{\cdot}C_6H_4{\cdot}OMe$-*p* is 140·5—141·5°. (Among the R_3SiX compounds with X = Cl, F, H, and OMe, those that are optically active have higher melting points than the racemic mixtures.) The optically active compounds are markedly more soluble in hexane than the racemic material, and thus their optical purity can be improved by recrystallization; in this way, for example, the specific rotation of the (+)-$R_3Si{\cdot}C_6H_4{\cdot}OMe$-*p* compound obtained

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[1] Part XXIX, Austin and Eaborn, *J.*, 1964, 2279.

[2] Frye, Thesis, Pennsylvania State Univ., 1960.

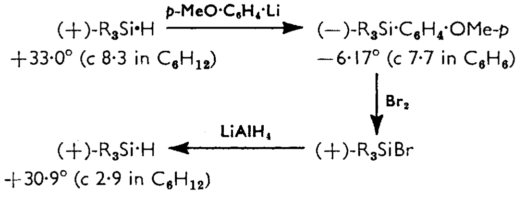
[3] Sommer and Frye, *J. Amer. Chem. Soc.*, 1959, **81**, 1013; 1960, **82**, 3796, 4118; U.S.P. 3,024,262/1962; Sommer, Frye, Musolf, Parker, Rodewald, Michael, Okaya, and Pepinsky, *J. Amer. Chem. Soc.*, 1961, **83**, 2210.

[4] Sommer, *Angew. Chem., Internat. Ed.*, 1962, **1**, 143.

from the chloride (—)-R_3SiCl was raised to $[\alpha]_D^{19}$ +6·13° (*c* 7·8 in benzene). The $R_3Si{\cdot}C_6H_4{\cdot}OMe$-*p* compounds having $[\alpha]_D^{20}$ in the range ±6·0—6·2° probably were of a high degree of optical purity, but presumably were not wholly free from racemic material, since their melting points were not sharp; certainly they must have been more than 92% optically pure in view of the results described below.

Since the formation of the (—)-R_3SiCl compound from the (+)-R_3SiH compound involves retention,[2-4] it is clear that the couplings of the hydride and chloride proceed with opposite stereochemistry.* It is known that reactions of the R_3SiCl compounds tend to go with inversion,[2-4] and those of R_3SiH and compounds with retention of configuration at the silicon atom,[4] and so it is probable that the $R_3Si{\cdot}C_6H_4{\cdot}OMe$-*p* compound is formed from the chloride with inversion and from the hydride with retention (compare refs. 6—8), and thus that $R_3Si{\cdot}C_6H_4{\cdot}OMe$-*p* and R_3SiH compounds of the same sign of rotation have the opposite configuration. It will be appreciated that the validity of the conclusions drawn below about the stereochemistry of the bromine cleavage reaction depend on the accuracy of the above assignments of configuration.

The bromine cleavage of the $R_3Si{\cdot}C_6H_4{\cdot}OMe$-*p* compound was carried out in carbon tetrachloride and in benzene. As the colour of the bromine disappeared the rotation of the solution changed in sign; for example, in benzene the rotation changed from that corresponding to $[\alpha]_D^{20}$ —6·17° (*c* 7·6) to that corresponding to $[\alpha]_D^{20}$ +13·4°, and in carbon tetrachloride the change was from $[\alpha]_D^{20}$ —3·29° (*c* 3·9) to $[\alpha]_D^{20}$ + 14·1° (in both cases the rotation subsequently decreased slightly during several days). Attempts to isolate the optically active bromide, R_3SiBr, were unsuccessful, and so the product from the cleavage in benzene was reduced with lithium aluminium hydride to give the hydride, R_3SiH (with inversion[3]). Thus from the (—)-$R_3Si{\cdot}C_6H_4{\cdot}OMe$-*p* compound, $[\alpha]_D^{20}$ —6·17° (*c* 7·7 in benzene), in benzene, the hydride, (+)-R_3SiH, $[\alpha]_D^{20}$ +30·9° (*c* 2·9 in cyclohexane), was obtained in 26% yield. Thus the Walden cycle shown in Scheme 1 had been accomplished with 92% overall retention of configuration. We conclude that the bromine cleavage involves at least 92% inversion of configuration and, since some loss of optical activity is almost certainly associated with other steps of the cycle (some racemization of the R_3SiBr compound before and during reduction being particularly likely), it is probable that the cleavage is stereospecific.



Scheme 1. (Rotations are $[\alpha]_D^{20}$.)

The reason for the low yield of the hydride, R_3SiH, from the cleavage is that side reactions occurred, which not only lowered the amount of R_3SiBr formed but also interfered with the subsequent isolation of the R_3SiH compound. Vapour-phase chromatography showed that cleavage of the (±)-$R_3Si{\cdot}C_6H_4{\cdot}OMe$-*p* compound by 1·0 mol. of bromine in

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* It is not known definitely (cf. ref. 5) whether the more lævorotatory (—)-menthoxide has the same or opposite configuration to that of the (+)-hydride, which is formed from it by reduction with lithium aluminium hydride. It is likely that the reduction proceeds with retention,[2-4] and thus that the more lævorotatory (—)-menthoxide has the same configuration as the (—)-$R_3Si{\cdot}C_6H_4{\cdot}OMe$-*p* compound. This would mean that the latter is formed from the menthoxide with retention, which would be consistent with the observation that reactions of Si–OR bonds occur commonly (though not always) with retention.[4]

[5] Brook and Peddle, *J. Amer. Chem. Soc.*, 1963, **85**, 1869.
[6] Brook and Warner, *Tetrahedron Letters*, 1962, 815.
[7] Sommer, Rodewald, and Parker, *Tetrahedron Letters*, 1962, 821.
[8] Sommer, Michael, and Korte, *J. Amer. Chem. Soc.*, 1963, **85**, 3712.

benzene gave 0·69 mol. of *p*-bromanisole,* 0·26 mol. of 1-bromonaphthalene, and 0·26 mol. of anisole. Again, from 1·2 mol. of bromine, were formed 0·80 mol. of *p*-bromanisole,* 0·23 mol. of 1-bromonaphthalene, and 0·19 mol. of anisole. It is evident that, not only did bromine cleavage of the Si–naphthyl bond compete with that of the Si–*p*-methoxyphenyl bond, but also some cleavage by hydrogen bromide occurred. It is likely that traces of water were responsible for the formation of some of the hydrogen bromide, and subsequent work by Mr. J. D. Austin, involving dry-box and vacuum-line techniques has reduced the amount of acid cleavage to about half of that indicated above but has not eliminated it. Some hydrogen bromide may be formed by bromination of the aryl groups present; anisole undergoes bromination under the reaction conditions but naphthalene does not react.

In an attempt to eliminate the concurrent acid cleavage, the bromine cleavage in benzene was carried out in the presence of approximately one equivalent of anhydrous pyridine. Pyridine hydrobromide separated and anisole could not be detected in the products, but most of the optical activity was lost. {Reduction gave the R_3SiH compound, $[\alpha]_D^{19}$ +0·16° (*c* 4·3 in cyclohexane), in 50% yield.} In a separate experiment, after bromine cleavage had been carried out in the usual way, to give a solution corresponding to a specific rotation of +14·7°, approximately one equivalent of pyridine was added; the rotation fell rapidly, indicating that the (+)-R_3SiBr compound is racemized by pyridine or pyridine hydrobromide.

To obtain further information about the hydrogen bromide cleavage, the (—)-$R_3Si{\cdot}C_6H_4{\cdot}OMe$-*p* compound was treated with 1·2 equivalents of hydrogen bromide in benzene; the rotation fell from that corresponding with $[\alpha]_D^{20}$ —6·24° to that corresponding with $[\alpha]_D^{20}$ +5·94° (*c* 7·54). Vapour-phase chromatography showed that 75% of the Si–*p*-methoxyphenyl bonds had been cleaved to give anisole, and 38% of the Si–naphthyl bonds to give naphthalene. After reduction by lithium aluminium hydride, the hydride R_3SiH, $[\alpha]_D^{20}$ +13·8° (*c* 3·2 in benzene), was isolated in 8% yield. It seems that cleavage of the Si–*p*-methoxyphenyl bond by hydrogen bromide involves predominant inversion of configuration; it is possible that it proceeds with stereospecific inversion, the loss of activity occurring subsequently with the bromide.

It will be appreciated that the bromine cleavage of the (—)-MePh(1-$C_{10}H_7$)Si·C_6H_4·OMe-*p* compound gives, in addition to the expected (+)-MePh(1-$C_{10}H_7$)SiBr compound, some 20% of the bromide MePhBrSi·C_6H_4·OMe-*p*, and the rotation of the solution indicates that the latter is formed optically active and dextrorotatory. Such a cleavage of the silicon–naphthyl bond provides a valuable method of obtaining new types of optically active organosilicon compounds from the Sommer–Frye compounds; indeed, since the preliminary announcement of our results,[9] Sommer, Michael, and Korte have successfully exploited the cleavage in this way.[8] They support our conclusion that bromine cleavage involves inversion.

Mechanism of the Bromine Cleavage.—The mechanisms of cleavage of aryl–silicon bonds by electrophilic reagents, including bromine, have been discussed.[10-12] For the cleavage by bromine in acetic acid, which is of first order in bromine at low halogen concentrations but of higher order at higher concentrations,[10] the simplest picture consistent with the facts is one in which an intermediate of type (I) is formed in the rate-determining step and destroyed in a subsequent step, presumably by nucleophilic attack of a solvent molecule at the silicon atom, the process being analogous to that accepted for molecular bromination of aromatic compounds in acetic acid.[13] The additional bromine molecules required in

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* Possibly contaminated with a little naphthalene (see the Experimental section).

[9] Eaborn and Steward, *Proc. Chem. Soc.*, 1963, 59.

[10] Eaborn and Webster, *J.*, 1957, 4449; 1960, 179.

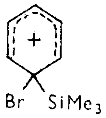
[11] Eaborn, " Organosilicon Compounds," Butterworths Scientific Publ., London, 1960, pp. 146—157; Eaborn and Pande, *J.*, 1960, 1566; Bott, Eaborn, and Greasley, *J.*, 1964, 4804.

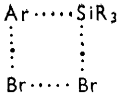
[12] Stock and Spector, *J. Org. Chem.*, 1963, **28**, 3272.

[13] de la Mare and Ridd, " Aromatic Substitution. Nitration and Halogenation," Butterworths Scientific Publ., London, 1959, pp. 122—128; Norman and Taylor, " Electrophilic Aromatic Substitution," Elsevier Publ. Co., Amsterdam, ch. 5. in the press.

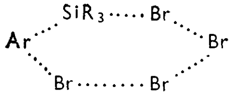
some cases by the kinetics [10] would then assist separation of the bromide ion involved in formation of the intermediate (I). However, the possibility of a four-centre process (II)

(I)





(II)



(III)

has also been suggested,[10,11] the availability of vacant *d*-orbitals on the silicon atom making plausible nucleophilic attack on silicon concerted with electrophilic attack at carbon.* [14] The fact that iodine monochloride is more effective than chlorine in the cleavage of aryl–silicon bonds in acetic acid has been interpreted by Stock and Spector as evidence for a four-centre process,[12] and Dessy and Paulik have suggested that such processes are common in reactions of organometallic compounds generally.[16]

If the bromine cleavage had this four-centre mechanism in acetic acid, such a process would be even more likely in carbon tetrachloride or benzene, since the solvent has no nucleophilic power and since any separation of ions, which is unlikely in the weakly polar reaction, would be avoided. However, such a mechanism would, we believe, involve retention of configuration at the silicon atom, and must thus be ruled out for the cleavage in benzene and carbon tetrachloride (and, by implication, for that in acetic acid also). The only other type of mechanism that the stereochemical result enables us to rule out is an unlikely one in which a free siliconium ion separates from an intermediate such as (I). We cannot rule out, however, the possibility that the aryl–silicon bond breaks to give a π-complex between the π-electrons of the ring and the siliconium ion before the latter is removed by nucleophilic attack, since this could result in stereospecific inversion. The simplest mechanism consistent with the results, in view of the analogy between the cleavage and aromatic bromination,[10] is one involving the formation (probably rate-determining) of an ion pair between the ion (I) and, say, the tribromide ion (this being suggested rather than the bromide ion, since the bromine cleavage of trimethylphenylsilane in carbon tetrachloride has been shown [17] to be of second order in bromine, at least at some concentrations of bromine), followed by nucleophilic attack on silicon by the tribromide ion before dissociation of the ion-pair. The nucleophilic attack to break the aryl–silicon bond could then be of the 180°- or 120°-type, represented by diagrams (A) and (B) (in which Y represents the entering group and X the leaving group) since both, we believe,[18] would lead to inversion.†

Although the four-centre process (II), involving the type of stereochemistry illustrated by diagram (C) or (D), is ruled out, we cannot exclude the possibility of the related cyclic

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* Where the kinetics require additional bromine molecules in the transition state,[10] these could be thought of as stabilizing the partly negative nucleophilic bromine atom in the transition state, the immediate reaction product possibly being the complex $R_3Si{\cdot}Br{\cdot}Br_2$ (see below, and compare ref. 15).

† Discussion of the significance of these diagrams, and demonstration of the suggested stereochemical consequences of the various possibilities for nucleophilic attack at silicon will be found in ref. 18. It should be noted that Sommer considers the stereochemical course of 120° attack to be in doubt.[4]

We have neglected mechanisms based on square-pyramidal (sp^2d^2) intermediates, since it seems to us these must be higher-energy structures than the trigonal bipyramid (sp^3d) intermediates (cf. ref. 19). Sommer and Rodewald recently proposed a square-pyramidal intermediate (but with the silicon atom not necessarily in the plane of the base) to explain the fact that in the presence of methanol the compound R_3SiF can be racemized without replacement of the fluorine.[20] If the racemization occurs, as they propose, without breaking and re-formation of the Si–F bond, then an acceptable explanation is that interchange of axial and equatorial positions occurs in an sp^3d type of intermediate, since there is evidence that this can be a rapid process.[19]

[14] Eaborn, "Organosilicon Compounds," Butterworths Scientific Publ., London, 1960, pp. 108—110.

[15] Bott, Eaborn, and Waters, *J.*, 1963, 681.

[16] Dessy and Paulik, *Bull. Soc. chim. France*, 1963, 1373; *J. Chem. Educ.*, 1963, **40**, 185.

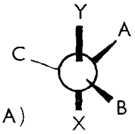
[17] Benkeser and Torkelson, *J. Amer. Chem. Soc.*, 1954, **76**, 1252.

[18] Baker, Bott, Eaborn, and Jones, *J. Organomet. Chem.*, 1963, **1**, 37.

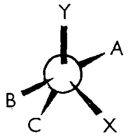
[19] Gillespie, *J.*, 1963, 4672, 4679.

[20] Sommer and Rodewald, *J. Amer. Chem. Soc.*, 1963, **85**, 3898.

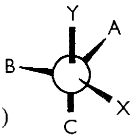
process (III). Indeed this is an attractive mechanism, since the Ar–SiMe$_3$–Br bond angle would be about 120°, which is consistent with a process of type (B) and thus, we think,



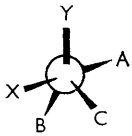
(A)



(B)



(C)



(D)

with inversion of configuration. The break-up of the complex (III) could be to give the aryl bromide and the complex R$_3$SiBr·Br$_2$ (analogous to the known[21] complex (C$_6$H$_{11}$)$_3$SiI·I$_2$; see also ref. 15), rather than the entities ArBr, R$_3$SiBr, and Br$_2$. The difference between the concerted process (III) and the ion-pair process, suggested above, involving 120°-type nucleophilic attack of tribromide ion on silicon within the ion pair, is rather fine, and experimental distinction between the two would be difficult.

EXPERIMENTAL

(+)-*Methyl-*1-*naphthylphenylsilane*, m. p. 63·5—64·5°, $[\alpha]_D^{21}$ +33·0° (*c* 8·3 in cyclohexane), was prepared by Frye's method.[2]

*Resolution of Methyl-*1-*naphthylphenylsilyl* (−)-*Menthyloxide.*—This compound was prepared and resolved by Frye's methods.[2] The more lævorotatory, less soluble diastereoisomer, had m. p. 84—85°, $[\alpha]_D^{22}$ −54·3° (*c* 11·3 in cyclohexane).

Preparation of (+)-, (−)-, *and* (±)-p-*Methoxyphenylmethyl-*1-*naphthylphenylsilane.*—(i) (+)-Methyl-1-naphthylphenylsilane (5·0 g., 0·020 mole), $[\alpha]_D^{21}$ +33·0° (*c* 8·3 in cyclohexane), was chlorinated in carbon tetrachloride.[2] The carbon tetrachloride was removed under reduced pressure, and the crystalline (−)-methyl-1-naphthylphenylchlorosilane obtained was taken up in ether (50 ml.). The ethereal solution was added during 15 min. to a solution of *p*-methoxyphenyl-lithium, prepared at 0° from *p*-bromoanisole (7·1 g., 0·040 mole), lithium foil (~0·5 g.), and ether (100 ml.). The mixture was refluxed for 8 hr., benzene (100 ml.) was added, and the mixture was poured on ice. The ethereal layer was separated, washed, dried (Na$_2$SO$_4$), and filtered, and the ether was replaced by benzene. The solution was passed through a column of silica gel, and the benzene was removed to leave a colourless syrup (7·0 g.), $[\alpha]_D^{19}$ +5·72 (*c* 7·8 in benzene). This was boiled with hexane while benzene was added dropwise until dissolution was complete, and the mixture was allowed to cool and set aside at room temperature. The crystals (0·6 g.) formed were filtered off, and had m. p. 70—140°, $[\alpha]_D^{20}$ +1·86° (*c* 7·1 in benzene). The filtrate was evaporated to give a solid, which was recrystallized twice from hexane at 0° to give (+)-*p*-methoxyphenylmethyl-1-naphthylphenylsilane, (5·3 g., 74%), m. p. 69·5—73·5°, $[\alpha]_D^{19}$ +6·13° (*c* 7·8 in benzene).

The above preparation was repeated, except that after the formation of the *p*-methoxyphenyllithium the ether was replaced by benzene, and the coupling with the chloride was carried out in this solvent. The crude product, $[\alpha]_D^{20}$ +5·21° (*c* 7·8 in benzene), was recrystallized to give (+)-p-*methoxyphenylmethyl-*1-*naphthylphenylsilane* (75%), m. p. 71—73·5°, $[\alpha]_D^{22}$ +6·00° (*c* 7·8 in benzene) (Found: C, 80·9; H, 6·1; Si, 8·1. C$_{24}$H$_{22}$OSi requires C, 81·3; H, 6·25; Si, 7·9%).

(ii) (±)-*p*-Methoxyphenylmethyl-1-naphthylphenylsilane was prepared by the above method with benzene as solvent. The intermediate (±)-chlorosilane was a syrup. Two crystallizations of the crude product from 1 : 1 benzene–hexane gave (±)-p-*methoxyphenylmethyl-*1-*naphthylphenylsilane* (75%), m. p. 140·5—141·5° (Found: C, 81·0; H, 6·4; Si, 8·0%).

(iii) (+)-Methyl-1-naphthylphenylsilane (5·0 g., 0·020 mole), $[\alpha]_D^{21}$ +33·0° (*c* 8·3 in cyclohexane), in ether (50 ml.) was added to a solution of *p*-methoxyphenyl-lithium prepared from *p*-bromoanisole (7·1 g., 0·040 mole) in ether (100 ml.). The mixture was refluxed for 8 hr., benzene (100 ml.) was added, and the mixture was added to ice. Separation, washing, drying, and evaporation of the organic layer left a syrup; this was passed in hexane through a column of silica gel and concentrated. The solid obtained was crystallized from hexane to give (−)-*p*-methoxyphenylmethyl-1-naphthylphenylsilane (77%), m. p. 70—73°, $[\alpha]_D^{19}$ −6·0° (*c* 7·7 in benzene) (Found: C, 81·2; H, 6·5; Si, 8·1%).

(iv) From (±)-methyl-1-naphthylphenylsilane, by the method described in (iii), except

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[21] Eaborn, *J.*, 1953, 4154.

that 1 : 1 benzene–hexane was used in place of hexane, (±)-*p*-methoxyphenylmethyl-1-naphthylphenylsilane, m. p. 140·5—141·5°, was obtained in 95% yield.

(v) The more lævorotatory enantiomer of (−)-menthyloxymethyl-1-naphthylphenylsilane (8·0 g., 0·020 mole), m. p. 84—85°, $[\alpha]_D^{21}$ −54·8° (*c* 12·7 in cyclohexane), in ether (40 ml.) was added to a solution of *p*-methoxyphenyl-lithium prepared from *p*-bromoanisole (7·1 g., 0·040 mole) in ether (100 ml.), and the mixture was refluxed for 8 hr. Benzene (100 ml.) was added and the mixture was poured on ice; the organic layer was separated, washed, dried, and concentrated, and the (−)-menthol was distilled off at reduced pressure. A solution of the remaining syrup in hexane was passed over silica gel, and concentrated to give crystals, which recrystallized from hexane to give (−)-*p*-methoxyphenylmethyl-1-naphthylphenylsilane (91%), m. p. 70—72°, $[\alpha]_D^{20}$ −6·17° (*c* 7·7 in benzene).

(vi) By the method described in (v) above, except that 1 : 1 benzene–hexane was used in place of hexane, from (±)-methyl-1-naphthylphenylsilyl (−)-menthyloxide was obtained (±)-*p*-methoxyphenylmethyl-1-naphthylphenylsilane (91%), m. p. 140—141°.

The infrared spectra of the samples of optically active and racemic *p*-methoxyphenylmethyl-1-naphthylphenylsilane in carbon tetrachloride were identical.

Cleavage of (−)-p-*Methoxyphenylmethyl*-1-*naphthylphenylsilane by Bromine.*—(*a*) *Purification of materials.* Reagent-grade bromine was stirred with several lots of concentrated sulphuric acid and distilled from the acid; it was then distilled, with the exclusion of atmospheric moisture, three times from anhydrous potassium bromide and twice from anhydrous calcium bromide. It was stored and transferred in a dry-box.

Spectral-grade carbon tetrachloride was refluxed with calcium hydride, from which it was distilled. It was stored over phosphorus pentoxide.

Reagent-grade benzene was refluxed with calcium hydride, from which it was distilled; it was stored over lithium aluminium hydride.

AnalaR pyridine was refluxed with and distilled from calcium hydride.

(b) *Stereochemistry of cleavage by bromine in benzene.* (−)-*p*-Methoxyphenylmethyl-1-naphthylphenylsilane (4·8 g., 0·0136 mole), $[\alpha]_D^{20}$ −6·17° (*c* 7·7 in benzene), was dissolved in benzene (50 ml.), and a solution of bromine (0·0162 mole) in benzene (14·5 ml.) was added. The bulk of the mixture was set aside in the dark, but a portion was placed in a polarimeter tube and the following equivalent specific rotations ($[\alpha]_D^{20}$, *c* 7·6) were noted: 45 min., +14·0°; 105 min., +13·1°; 180 min., +13·4° (readings before 45 min. were not possible because of the colour of the bromine). After 3 hr., the mixture was added rapidly to lithium aluminium hydride (2 g., 0·053 mole) in ether (100 ml.). The mixture was stirred for 0·5 hr., then carefully added to a mixture of concentrated hydrochloric acid (30 ml.), ice water (500 ml.), and benzene (50 ml.). The organic layer was separated, washed, dried (Na_2SO_4), and filtered, and solvent was removed from the filtrate under reduced pressure. The syrup formed was taken up in pentane (25 ml.); the solution was passed through a column of silica gel, and the column was washed with additional pentane (300 ml.). The pentane was removed under reduced pressure to leave a syrup, which was crystallized from pentane, first at −80° and then at −15° to give (+)-methyl-1-naphthylphenylsilane (0·88 g., 0·0036 mole, 26%), m. p. 58·5—62°, $[\alpha]_D^{20}$ +30·9° (*c* 2·9 in cyclohexane); the infrared spectrum was identical with that of an authentic sample. Washing of the silica gel column with more pentane gave no more of the organosilane.

(*c*) *Products from cleavage by bromine in benzene.* (±)-*p*-Methoxyphenylmethyl-1-naphthylphenylsilane was submitted to the cleavage procedure described in (*b*) above. The reaction mixture was then shaken with water (or if bromine were still present, dilute sodium thiosulphate), and the organic layer was separated and dried (Na_2SO_4). A suitable amount of an internal standard (*p*-chloroanisole, *p*-bromoanisole, or s-butylbenzene) was added to a measured volume of the solution, and samples were injected into a 4 m. column of 80—100 mesh Embacell coated with Embaphase silicone oil. Argon was used as carrier gas, and the detector was of the β-ray ionization type. A column temperature of 110° was used for anisole, and one of 136° for the other products. Standard solutions were used for calibrations, and yields of products could be determined, we believe, within ±5%. Naphthalene could not be satisfactorily separated from *p*-bromoanisole, and the reported yields of the latter may thus be slightly high, though this uncertainty is probably within the overall ±5% mentioned above.

Analysis of the products from the above cleavage showed that 19% of the Si–C_6H_4·OMe-*p* bonds had been cleaved to give anisole and 80% to give *p*-bromoanisole, and 23% of the Si–naphthyl bonds had been cleaved to give 1-bromonaphthalene.

(*d*) *Cleavage by bromine in carbon tetrachloride.* To (−)-*p*-methoxyphenylmethyl-1-naphthylphenylsilane (0·51 g., 0·00144 mole), $[\alpha]_D^{19}$ −6·09° (*c* 7·6 in benzene), $[\alpha]_D^{20}$ −3·29° (*c* 5·1 in carbon tetrachloride), in carbon tetrachloride (10·0 ml.) was added bromine (0·00145 mole) in carbon tetrachloride (3·0 ml.). Some of the solution was transferred to a polarimeter tube, and the following equivalent specific rotations ($[\alpha]_D^{20}$, *c* 3·9) were noted: 3 hr., +14·1°; 7 hr., +14·1°. After 7 hr., the solvent was removed under reduced pressure to give a syrup with a very small optical rotation, indicating that racemization of the bromide had occurred.

Gas-chromatographic analysis of products from similar cleavage of racemic starting material showed that the yields were, within experimental error, the same as those for the reaction in benzene.

(*e*) *Cleavage by bromine in presence of pyridine.* To a solution of (−)-*p*-methoxyphenylmethyl-1-naphthylphenylsilane (4·98 g., 0·0140 mole), $[\alpha]_D^{20}$ −6·24° (*c* 10·0 in benzene), and pyridine (1·11 g., 0·0140 mole) in benzene (50 ml.) was added a 1·35M-solution (12·44 ml.) of bromine in benzene, and the bulk of the mixture was set aside in the dark. Observations on a small portion showed that the equivalent specific rotations ($[\alpha]_D^{20}$, *c* 8·0 in benzene) were: 1·5 hr., +0·5°; 4 hr., +0·8 (the presence of a precipitate of pyridine hydrochloride lowered the accuracy of the readings). The bulk of the mixture after 4 hr. was treated as described in section (*b*), yielding (±)-methyl-1-naphthylphenylsilane (50%), m. p. 40·5—42·5°, $[\alpha]_D^{19}$ +0·16 (*c* 4·3 in cyclohexane). The infrared spectrum was identical with that of an authentic sample, m. p. 40—42°.

Vapour-phase chromatographic analysis of the mixture obtained by similar cleavage of (±)-*p*-methoxyphenylmethyl-1-naphthylphenylsilane indicated that 53% of the silicon–*p*-methoxyphenyl bonds had given *p*-bromoanisole and none had given anisole, and 19% of the silicon–naphthyl bonds had given 1-bromonaphthalene.

In a separate experiment, the bromine cleavage was carried out as described in section (*b*), to give a solution with rotation equivalent to $[\alpha]_D^{20}$ +14·7° (*c* 6·7). One equivalent of pyridine was then added, and the equivalent specific rotation dropped rapidly. After 4 hr. it was +1·85°, and little further change occurred in a further 8 hours.

Cleavage by Hydrogen Bromide in Benzene.—Hydrogen bromide was prepared by the action of anhydrous bromine on anhydrous 1,2,3,4-tetrahydronaphthalene.[22] The gas was passed through 1,2,3,4-tetrahydronaphthalene, then over anhydrous calcium bromide, and was finally dissolved in benzene. The solution was standardized and stored in a dry-box.

The hydrogen bromide cleavage was carried out essentially by the method for bromine cleavage described in section (*b*), above, except that all the manipulations before the hydrolysis were carried out in a dry-box. Thus an 0·675M-solution of hydrogen bromide in benzene (30·3 ml.) was mixed with a solution of (−)-*p*-methoxyphenylmethyl-1-naphthylphenylsilane (6·06 g., 0·0171 mole), $[\alpha]_D^{20}$ −6·24° (*c* 10·0 in benzene), in benzene (50 ml.) and the mixture was set aside in the dark for 4·5 hr.; equivalent specific rotations, $[\alpha]_D^{20}$, were: *ca.* 8 min., −0·9°; 0·5 hr., +2·13°, 1·5 hr., +4·80°; 3·5 hr., +5·89°; 4·5 hr., +5·94°. Reduction with lithium aluminium hydride and the usual working-up, gave impure (+)-methyl-1-naphthylphenylsilane (0·35 g., 0·0014 mole, 8·2%), m. p. 40—60°, $[\alpha]_D^{20}$ +13·8° (*c* 3·2 in benzene); infrared analysis confirmed that the product was mainly this organosilane but showed that some other material was also present.

Vapour-phase chromatographic analysis of the products from similar cleavage of racemic starting material showed that 75% of the Si–C_6H_4·OMe bonds had been cleaved to give anisole and 38% of the Si–$C_{10}H_7$ bonds to give naphthalene.

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[22] Duncan, *Inorg. Synth.*, 1939, **1**, 151.