Correlation of Configuration of Some Organosilanes

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A series of chemical interconversions are described which supplement evidence obtained previously for assignment of configuration to (−)-mesitylmethoxymethylphenylsilane, (−)-benzyl(methoxy)(methyl)phenylsilane, and (−)-isopropyl(methoxy)(methyl)phenylsilane. The reaction of bromine with (+)-mesitylmethylphenyl-1-naphthylsilane has been shown to lead to formation of bromo(methyl)-1-naphthylphenylsilane and mesityl bromide in good yield and with a high degree of stereospecificity.

We have reported[1] on the preparation of some new optically active organosilanes by partial reduction of methoxysilanes with chiral reducing complexes, and have proposed tentative assignments of configuration based primarily on optical rotation studies. In the present work we describe a series of chemical interconversions which provide further evidence for configurational assignments. These chemical interconversions are outlined in the Scheme which shows the configurations, including those already known and those

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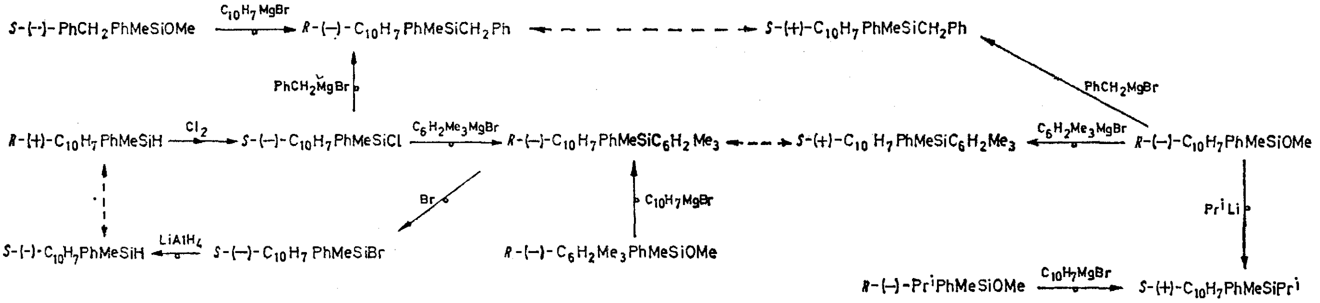
[1] A. Holt, A. W. P. Jarvie, and G. J. Jervis, *J.C.S. Perkin II*, 1973, 114.

here inferred, of the compounds concerned, and the steric course of the interconversions.

A key step in establishing the configuration of the compounds with which we are concerned is the reaction of a methoxysilane with a Grignard reagent. There are relatively few examples in the literature where the steric course of such a reaction has been established, and it appears to vary according to the nature of the Grignard reagent involved. Whereas ethylmagnesium bromide reacts with methoxy(methyl)-1-naphthylphenylsilane with retention of configuration benzylmagnesium bromide reacts with this methoxysilane with inversion of configuration.[2] We show below that mesitylmagnesium bromide reacts with this same methoxysilane with inversion of configuration, and we assume that this steric pathway is general for reactions of aryl Grignard reagents with methoxysilanes.



SCHEME The symbols $\twoheadrightarrow$ and $\xrightarrow[o]{}$ denote reactions proceeding with specific retention and specific inversion of configuration, respectively. The symbol $\leftarrow - - - \rightarrow$ denotes an enantiomeric relationship. $C_{10}H_7$ = 1-Naphthyl, $C_6H_2Me_3$ = mesityl

The configuration of (—)-mesityl(methyl)-1-naphthylphenylsilane may be established by two metods. The first is its formation from (—)-chloro(methyl)-1-naphthylphenylsilane, of known configuration, and mesitylmagnesium bromide. The assignment of an inversion pathway to this reaction is in accordance with similar reactions [2] in the literature. The second method is by bromodearylation [3] to give (—)-bromo(methyl)-1-naphthylphenylsilane, whose configuration is also known. The cleavage of the mesityl group from silicon is assumed to proceed with inversion of configuration by analogy with the cleavage of other aryl groups [3,4] from silicon. If, on the basis of this evidence, we accept the configuration of (—)-mesityl(methyl)-1-naphthylphenylsilane as established then the formation of its enantiomer by reaction of mesitylmagnesium bromide with (—)-methoxy(methyl)-1-naphthylphenylsilane shows conclusively that this particular reaction of an aryl Grignard reagent with a methoxysilane proceeds with inversion of configuration. If we assume that 1-naphthylmagnesium bromide reacts with (—)-mesityl(methoxy)(methyl)phenylsilane with inversion of configuration this latter compound may be assigned the *R*-configuration.

The reaction of 1-naphthylmagnesium bromide with (—)-benzyl(methoxy)(methyl)phenylsilane gives (+)-benzyl(methyl)-1-naphthylphenylsilane, whose configuration is known,[5] and if we assume that this reaction proceeds with inversion of configuration then this methoxysilane may be assigned the *S*-configuration.

The configuration of (—)-isopropyl(methyl)-1-naphthylphenylsilane follows from its formation by reaction of (—)-chloro(methyl)-1-naphthylphenylsilane and isopropylmagnesium bromide. This reaction is assumed to proceed with inversion of configuration by analogy with similar reactions.[2] If the reaction of 1-naphthylmagnesium bromide with (—)-isopropyl(methoxy)(methyl)phenylsilane is assumed to proceed with inversion of configuration this latter compound may be assigned the *R*-configuration.

The configurational assignments suggested here are largely complementary to those suggested earlier.[1] For benzyl(methoxy)(methyl)phenylsilane, benzyl(methyl)phenylsilane, mesityl(methoxy)(methyl)phenylsilane and mesityl(methyl)phenylsilane we have a self-consistent set of assignments, if we now accept that the sign of the Cotton effect around 281 nm (see discussion in ref. 1) is not a reliable guide to configuration of arylsilanes. The configurational assignment here suggested for isopropyl(methoxy)(methyl)phenylsilane is opposite to that originally [1] proposed. We believe that our present assignment is more likely to be correct.

The reaction of mesityl(methyl)-1-naphthylphenylsilane with bromine was of great interest. Cleavage of aryl groups from silicon by reagents such as bromine and acids can logically be interpreted [6] as an aromatic substitution reaction in which the silicon is displaced by an electrophile. Whilst the relative rates of cleavage of most common aryl groups from silicon by bromine have been established such studies do not appear to have included mesityl groups. Perchloric acid cleaves mesityl groups rapidly from silicon [7] and the relative rates of nitration of various hydrocarbons [8] would also suggest

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[2] L. H. Sommer and W. D. Korte, *J. Amer. Chem. Soc.*, 1967, **89**, 5802.

[3] C. Eaborn and O. W. Steward, *Proc. Chem. Soc.*, 1963, 59; *J. Chem. Soc.*, 1965, 521.

[4] L. H. Sommer, K. W. Michael, and W. D. Korte, *J. Amer. Chem. Soc.*, 1963, **85**, 3712.

[5] A. Brook and W. W. Limburg, *J. Amer. Chem. Soc.*, 1963, **85**, 832.

[6] C. Eaborn, 'Organosilicon Compounds,' Butterworths, London, 1960, pp. 146—157.

[7] C. Eaborn and R. C. Moore, *J. Chem. Soc.*, 1959, 3640.

[8] S. R. Hartshorn and K. Schofield, 'Some Aspects of Recent Work on Nitration,' in 'Progress in Organic Chemistry,' eds. W. Carruthers and J. K. Sutherland, Butterworths, London, 1973, vol. 8.

that cleavage of silicon–mesityl linkages by electrophiles should be particularly rapid. Our results confirm these expectations. Using stoicheiometric quantities of bromine the mesityl group is smoothly cleaved from mesityl(methyl)-1-naphthylphenylsilane to give bromo(methyl)-1-naphthylphenylsilane. G.l.c. shows that bromomesitylene is produced virtually quantitatively with only a trace of bromonaphthalene. The cleavage of naphthyl groups from silicon by bromine has been shown to be highly stereospecific and this reaction has been the basis for the preparation of several new optically active organosilanes. Our results indicate that the cleavage of the mesityl group is also highly stereospecific and the way would appear to be open for the preparation of optically active organosilanes with two groups (mesityl and 1-naphthyl) which may, in sequence, be replaced by other groups by stereospecific reactions. The synthetic applications of these reactions are being investigated.

EXPERIMENTAL

60 MHz ^{1}H N.m.r. spectra were obtained on a Perkin-Elmer R10 spectrometer operating at 35°. 100 MHz Spectra were obtained on a Perkin-Elmer R14 spectrometer. Tetramethylsilane was used as internal standard throughout. I.r. spectra were obtained on a Perkin-Elmer 137G Infracord spectrophotometer. G.l.c. analyses were carried out on a Pye series 104 chromatograph with a katharometer detector, helium as carrier gas, and a silicone gum stationary phase. Light petroleum of b.p. 60—80° was used throughout. Column chromatography was carried out on silica gel using benzene–light petroleum as eluant. All preparations of and reactions with organomagnesium and organolithium compounds were carried out under nitrogen. Optically active methoxy(methyl)-1-naphthylphenylsilane, -mesitylphenylsilane, -benzylphenylsilane, and -phenylisopropylsilane were prepared as previously described.[1]

Preparation of (+)-(S)-*Mesityl(methyl)*-1-*naphthylphenylmethylsilane*.—A solution of (−)-(*R*)-methoxy(methyl)-1-naphthylphenylsilane (2.78 g, 0.01 mol; $[\alpha]_D$ −1.0°) in dry toluene (25 ml) was added to mesitylmagnesium bromide prepared from bromomesitylene (3 g, 0.015 mol) dissolved in diethyl ether (70 ml). After heating under reflux for 24 h little reaction appeared to have taken place. Toluene (100 ml) was added and ether (45 ml) removed by distillation. The resulting solution was heated under reflux for seven days. After work-up and chromatography the product (0.96 g, 26.5%) had $[\alpha]_D$ +2.16° (*c* 1.92, hexane). After recrystallisation from pentane it had m.p. 74—75°, τ (60 MHz; CCl_4) 9.45 (3 H, s), 7.85 (3 H, s), 7.75 (6 H, s), 3.30 (2 H, s), and 2.70 (12 H, m), $\nu_{max.}$ 1 510, 1 430s, 1 255s, 1 220, 1 148s, 1 115, 985s, and 740s cm^{-1}.

Conversion of (−)-(R)-*Mesityl(methyl)*-1-*naphthylphenylsilane to* (−)-(S)-*Methyl*-1-*naphthylphenylsilane*.—Pure bromine (1.76 g, 0.011 mol) in carbon tetrachloride (2.5 ml) was added rapidly to (+)-mesityl(methyl)-1-naphthylphenylsilane (4.0 g, 0.011 mol) in carbon tetrachloride (10 ml) at −10°. After 5—10 min the colour had almost completely disappeared. Examination of the solution by g.l.c. showed that bromomesitylene had been formed almost quantitatively and that only a trace of 1-bromonaphthalene was present. The solution was added to a suspension of lithium aluminium hydride (1.04 g) in diethyl ether (20 ml) and the mixture stirred for 5 min at room temperature. After work-up the product (2.32 g, 84%) was recrystallised several times from hexane and had m.p. 61°, $[\alpha]_D$ −29.4° (*c* 0.24, hexane). Its i.r. spectrum was identical with that of a pure reference compound.

Preparation of (−)-(R)-*Mesityl(methyl)*-1-*naphthylphenylsilane from* (−)-(R)-*Mesityl(methoxy)(methyl)phenylsilane*.—A solution of (−)-(*R*)-mesityl(methoxy)(methyl)phenylsilane ($[\alpha]_D$ −0.92°; 2.7 g, 0.01 mol) in toluene (25 ml) was added to 1-naphthylmagnesium bromide (0.018 mol) in toluene (25 ml) and the mixture heated under reflux for seven days. After work-up the product was chromatographed to give (−)-(*R*)-mesityl(methyl)-1-naphthylphenylsilane (1.24 g, 34%). After recrystallisation from pentane it had m.p. 68°, $[\alpha]_D$ −0.97° (*c* 2.14, hexane). Its i.r. spectrum was identical with that of its enantiomer described above.

Preparation of (−)-(R)-*Mesityl(methyl)*-1-*naphthylphenylsilane from* (+)-(R)-*Methyl*-1-*naphthylphenylsilane*.—(−)-Chloro(methyl)-1-naphthylphenylsilane was prepared from (+)-methyl-1-naphthylphenylsilane (2.48 g, 0.01 mol) by the method of Sommer.[9] The carbon tetrachloride solvent was removed and replaced by ether (25 ml). The solution was added to a solution of mesitylmagnesium bromide (0.01 mol) in ether (50 ml) and the mixture heated under reflux for 24 h. After work-up the product (2.24 g, 62%) was chromatographed and recrystallised from pentane when it had m.p. 69—71°, $[\alpha]_D$ −3.21° (*c* 3.72, hexane). The i.r. spectrum was identical with those of products prepared by alternative routes described above.

Preparation of (+)-(S)-*Benzyl(methyl)*-1-*naphthylphenylsilane from* (−)-(R)-*Methoxy(methyl)*-1-*naphthylphenylsilane*.—This was prepared by reaction of (−)-methoxy(methyl)-1-naphthylphenylsilane with benzylmagnesium bromide by the method of Sommer.[2] The product after column chromatography and recrystallisation from pentane had m.p. 65—66°, $[\alpha]_D$ +1.8° (*c* 1.92, hexane).

Preparation of (−)-(R)-*Benzyl(methyl)*-1-*naphthylphenylsilane from* (−)-(S)-*Benzyl(methoxy)(methyl)phenylsilane*.—A solution of (−)-benzyl(methoxy)(methyl)phenylsilane (2.42 g, 0.01 mol; $[\alpha]_D$ −0.81°) in diethyl ether (25 ml) was added to a solution of 1-naphthylmagnesium bromide (0.15 mol) in diethyl ether and the mixture was heated under reflux for three days. After work-up the product was chromatographed and recrystallised from pentane, when it had m.p. 62—64°, $[\alpha]_D$ −0.8°. The i.r. spectrum was identical with that of the product from the previous experiment.

Preparation of (−)-(R)-*Benzyl(methyl)*-1-*naphthylphenylsilane from* (−)-*Chloro(methyl)*-1-*naphthylphenylsilane*.—(+)-Methyl-1-naphthylphenylsilane (2.48 g, 0.01 mol) was converted to the chlorosilane, as described above, and the solution in diethyl ether (25 ml) was added to benzylmagnesium chloride (0.01 mol) in diethyl ether (20 ml). The mixture was allowed to stand for 24 h at room temperature. After work-up, chromatography, and re-crystallisation from pentane the product (2.1 g, 62%) had m.p. 74°, $[\alpha]_D$ −2.4°. The i.r. spectrum was identical with those of the enantiomeric products described above.

Preparation of (+)(S)-*Isopropyl(methyl)*-1-*naphthylphenylsilane from* (−)-(R)-*Methoxy(methyl)*-1-*naphthylphenylsilane*.—A solution of (−)-(*R*)-methoxy(methyl)-1-naphthylphenylsilane ($[\alpha]_D$ —1.2°; 2.78 g, 0.01 mol) in diethyl ether (50 ml)

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

was added to isopropyl-lithium (0.015 mol) in diethyl ether (25 ml) and the mixture heated under reflux for seven days. After work-up the product was chromatographed to give (+)-(*S*)-isopropyl(methyl)-1-naphthylphenylsilane (1,2 g, 23%) which crystallised on standing, m.p. 51°, $[\alpha]_D$ +0.27°, τ (60 MHz; CCl_4) 9.73 (3 H, s), 9.3—8.6 (7 H, m), and 2.9—2.2 (12 H, m).

Preparation of (+)(S)-*Isopropyl*(*methyl*)-1-*naphthylphenylsilane from* (—)-(R)-*Isopropyl*(*methyl*)*phenylsilane*.—A solution of (—)-(*R*)-isopropyl(methoxy)(methyl)phenylsilane ($[\alpha]_D$ —3.72°; 1.94 g, 0.01 mol) in diethyl ether (20 ml) was added to a solution of 1-naphthylmagnesium bromide (0.01 mol) in diethyl ether (20 ml) and the mixture heated under reflux for seven days. After work-up the product was chromatographed (0.79 g, 27%) and had $[\alpha]_D$ +0.42°. It crystallised on standing, m.p. 54°, and had an i.r. spectrum identical with the material from the previous preparation.

Action of Bromine on (+)-*Benzyl*(*methyl*)-1-*naphthylphenylsilane*.—Purified bromine (16.0 g) in benzene (10 ml) was added rapidly to (±)-benzyl(methyl)-1-naphthylphenylsilane (33.8 g, 0.1 mol) and the mixture allowed to stand at room temperature until the colour had almost disappeared. After removal of the solvent the crude product was stirred with lithium aluminium hydride (1.2 g) in diethyl ether (25 ml) for 5 min and the excess of hydride was then destroyed. Examination by g.l.c. revealed the presence of four major components. Chromatography of reference compounds showed that one component (*ca.* 10% of the total) was 1-bromonaphthalene, but bromobenzene and benzyl bromide were absent.

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