ORGANOSILICON COMPOUNDS

XXIV*. THE STEREOCHEMISTRY OF METHOXYL EXCHANGE AT THE SILICON ATOM

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INTRODUCTION

The important work by Sommer and Frye has made available optically active α-$C_{10}H_7$ MePhSiX compounds ($C_{10}H_7$ = naphthyl), which have been employed extensively in studies of the stereochemistry of substitution at a silicon atom[2-10]. We now describe a study of the stereochemistry of the methoxyl exchange between the compound α-$C_{10}H_7$ MePhSiOMe and methanol, either "neutral" (see below) or containing acid or base catalysts.

RESULTS AND DISCUSSION

Optically active (—)-methoxymethyl-α-naphthylphenylsilane was prepared by Sommer and Frye's method involving reaction of methanol with methyl-α-naphthylphenylchlorosilane in pentane in the presence of cyclohexylamine[10], but the methanol used was labelled with tritium in the methyl group. The rates of detritiation and racemization were measured for solutions of the tritiated (—)-methoxide in methanol at 25°, either alone or in presence of catalysts, and the results are as follows.

"Neutral" methanolysis

Methanolysis was found to be slow in purified methanol, but the rate was sensitive to traces of impurities. Different rates were obtained in successive experiments with the same batch of solvent, probably, we think, because of traces of catalysts from the glass reaction vessel. It was thus necessary to determine the rates of racemization and of detritiation on the same solution in the same vessel, and when this was done the rate of detritiation was half the rate of racemization within the experimental uncertainty imposed by the fact that the rotation, R, could not be measured to better than $\pm$ 0.005°. Fig. 1 shows typical plots of log D_t against t (where D_t is a measure of the amount of tritium remaining in the methoxide at time t), and of log R_t against t (where R_t is the observed rotation); the scales of log R and log D have been made to differ by a factor of two (to compensate for the fact that the rate of racemization is twice the rate of inversion) and their origins have been moved to allow the two plots to coincide. The size of the circle around each polarimetrically-determined point

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[*] For Part XXIII see ref. 1.

indicates, for rotations of less than 0.2°, the effect of an error of ± 0.005° in the polarimeter reading R. Both plots are straight lines within the experimental error. While the rates of detritiation and of inversion (half the rate of racemization) always agreed to within ± 5 % in the first 40 % of the exchange reaction (80 % of the racemization), the mean first order rate constant for apparently identical runs varied from 5.9×10^{-7} to 7.2×10^{-7} sec^{-1}. We regard the figure of 5.9×10^{-7} sec^{-1} as an indication of the maximum rate of exchange in neutral methanol, for with further purification of the solvent and with more elaborate handling procedures even lower rates might be obtained.

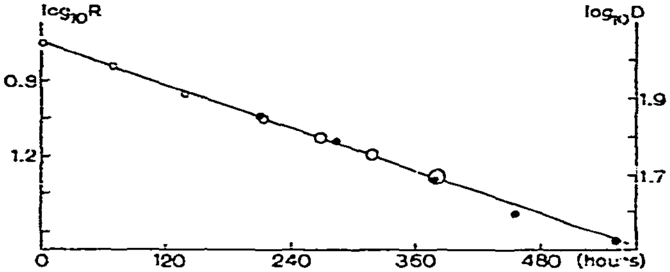

Fig. 1. Plots of log D against t (black circles) and of log R against t (open circles) for exchange in neutral methanol.

Acid catalysis

In the presence of *ca.* 1×10^{-3} M benzoic acid, methanolysis was about 150 times faster than in "neutral" solution. Again detritiation and racemization were first order, and the rate of detritiation and half the rate of racemization agreed within experimental error throughout each run; they agreed to within ± 1.5 % during the first 40 % of the exchange reaction.

Base catalysis

In the presence of *ca.* 1.45×10^{-3} M sodium acetate, the rate of methanolysis was approximately 12 times greater than that of the uncatalysed reaction. Again the reactions were first order, and the rate of detritiation and half the rate of racemization coincided within experimental error, although the mean rate constant varied between 64×10^{-7} and 85×10^{-7} sec^{-1} in apparently identical reactions.

With *ca.* 4×10^{-5} to 6×10^{-5} M sodium methoxide present, methanolysis was 40 to 300 times as fast as in neutral solution. The runs were not first order, however, the rate constants falling off as reaction proceeded, probably as methoxide was removed by reaction with some acidic species from the methanol, the glass, or the atmosphere. We did not investigate this behaviour further, because once again the rate of detritiation and half the rate of racemization coincided within experimental error (see Fig. 2), which is all we wished to establish.

We conclude that the rates of detritiation and of inversion (half the rate of racemization) are the same within experimental error under all the conditions of reaction. Because of the experimental error we cannot be sure that inversion is not a little slower than the exchange (it is unlikely, of course, to be faster), but it seems probable that effectively every act of substitution (exchange) is accompanied by inversion. The most likely explanation of this is that in all cases the forming Si–O bond is at 180° to the breaking Si–O bond, in a process rather similar to that in *S*N2 substitution at carbon, though with some participation of the 3d orbitals of silicon

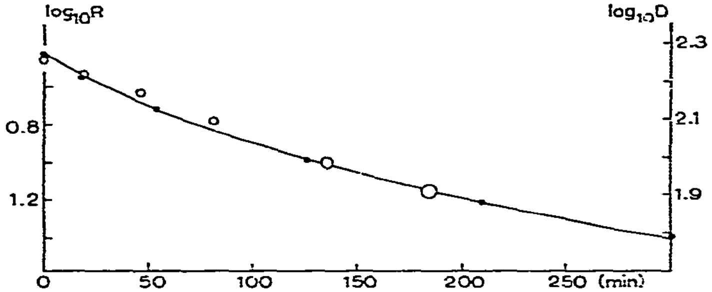

Fig. 2. Plots of log *D* against *t* (black circles) and of log *R* against *t* (open circles) for exchange catalysed by sodium methoxide.

(cf. ref. 11). The mechanisms are presumably as shown in sequences (1) to (3), though some or all of the sp^3d-hybridized intermediates may have no real existence (cf. ref. 11).

(1) $MeOH + R_3SiOMe^* \rightleftharpoons [Me(H)O^+\cdots Si^-R_3\cdots OMe^*] \rightleftharpoons [MeO\cdots Si^-R_3\cdots O^+(H)Me^*] \rightleftharpoons MeOSiR_3 + {}^*MeOH$

(2) $MeO^+H_2 + R_3SiOMe^* \rightleftharpoons R_3SiO^+(H)Me^* + MeOH$
$MeOH + R_3SiO^+(H)Me^* \rightleftharpoons [MeO\cdots Si^-R_3\cdots O^+(H)Me^*] + H^+$
$[MeO\cdots Si^-R_3\cdots O^+(H)Me^*] \rightleftharpoons [MeO\cdots Si^-R_3\cdots OMe^*] + H^+$
$[MeO\cdots Si^-R_3\cdots OMe^*] + H^+ \rightleftharpoons [Me(H)O^+\cdots Si^-R_3\cdots OMe^*]$
$[Me(H)O^+\cdots Si^-R_3\cdots OMe^*] + H^+ \rightleftharpoons [Me(H)O^+\cdots SiR_3 + Me^*OH$
$[Me(H)O^+\cdots SiR_3 + MeOH \rightleftharpoons MeO^+H_2 + R_3SiOMe$

(3) $MeO^- + R_3SiOMe^* \rightleftharpoons MeOSi^-R_3OMe^* \rightleftharpoons MeOSiR_3 + Me^*O^-$

That the Y–Si and Si–X bonds (where Y and X are the entering and leaving groups) are in a line in the transition state is not, however, the only possible explanation of inversion in substitution at silicon. If the reaction goes through a sp^3d-hybridized intermediate, the Si–Y and Si–X bonds in the intermediate can be at 180°, 120°, or 90° to each other, as in sequences (A), (B) and (C).* (These are the paths which involve the simplest and smallest bond movements: others may be devised which are more complicated and less likely.) Sequence (A) necessarily results in inversion, but so also, we suggest, does sequence (B), for if the group X is removed from the intermediate, collapse to the inverted product results as shown. Except that there might be some tendency for the three organic groups to be as far from each other as possible in the sp^3d-hybridized intermediate and thus to occupy the equatorial position, the observed inversions can be attributed to backside attack rather than 120° attack only on the grounds of simplicity and by analogy with reactions at carbon.

There are two ways in which the Si–Y and Si–X can be at right angles to each other, depending on whether Y or X is at the apex of the intermediate. Formation and collapse of either will lead, we suggest, to retention of configuration [sequences (Ci) and (Cii)].

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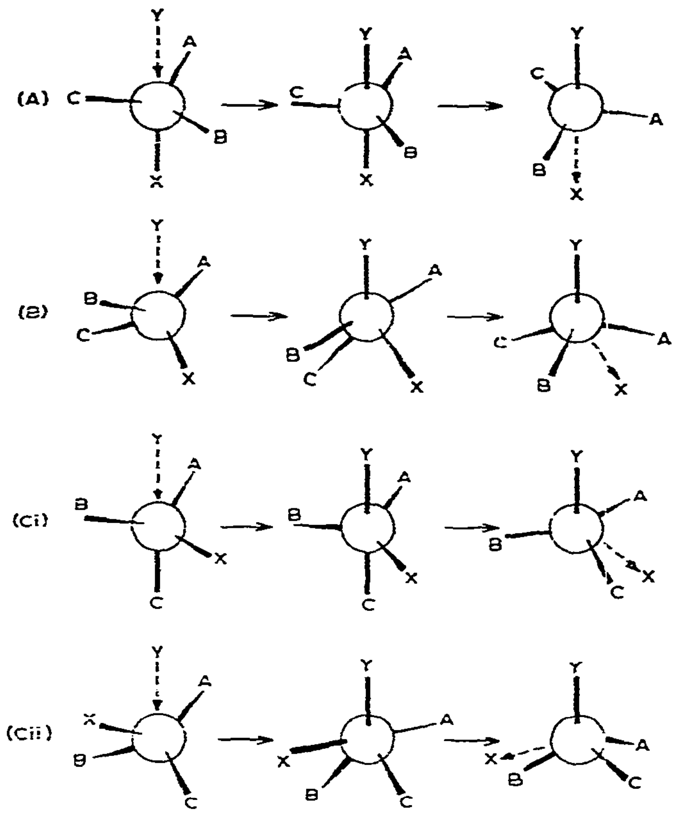
* We neglect the possibility of sp^2d^2 intermediates, since they would be less stable.



EXPERIMENTAL

Sommer and Frye's methods[10] were used to obtain (+)-methyl-α-naphthylphenylsilane and to convert it to (—)-methoxymethyl-α-naphthylphenylsilane, but methanol labelled with tritium in the methyl group[12,13] was employed.

The solvent methanol was dried by the method of Lund and Bjerrum[14] and fractionated from magnesium methoxide through a 40-plate Dixon-gauze column into a 2 l flask from which it was dispensed by pressure of nitrogen.

Rate measurements

(—)-Methoxymethyl-α-naphthylphenylsilane (0.4 to 0.5 g) was dissolved in methanol (30 to 40 g) in a polyethylene-stoppered flask in a thermostat-bath at 25°. Catalyst (if any) was added after 20 min, and after a further 30 min the first aliquots were withdrawn.

(i) The rotation was measured using a 2 dm end-filling micro-tube (capacity *ca.* 2.5 ml) in a Hilger "Microptic" polarimeter, model M413, graduated in 0.01° divisions.

(ii) For the tritium counting, 2 ml of solution were pipetted into 20 ml of scintillator solution (a toluene solution of terphenyl and wavelength shifter) and shaken immediately with 150 ml of aqueous ammonium chloride solution (5 g/l). The toluene layer was washed three times with water and dried (Na_2SO_4); 20 ml of it was pipetted into a counting cell and the radioactivity measured by the techniques previously described[15].

In the following sample runs R is in degrees, D (the galvanometer scale deflection) is in mm, and the reaction rates have been determined graphically in accordance with the equations:

$$k_{(exchange)} = \frac{2.303}{t}\log_{10}\frac{D_0}{D} \qquad k_{(inversion)} = \frac{2.303}{2t}\log_{10}\frac{R_0}{R}$$

Neutral solution

(i) 0.5353 g silane in 50 ml solution.

t (h)	0	46.00	112.4	187.6	268.0
R	0.340	0.275	0.190	0.130	0.085

$k_{inv} = 7.2 \times 10^{-7}$ sec^{-1}

t (h)	0	91.0	169.0	265.5	331.0
D	123.0	94.6	77.2	64.0	53.2

$k_{ex} = 7.06 \times 10^{-7}$ sec^{-1}

Benzoic acid solution

(i) 0.3826 g silane in 29.05 g solution 1.1 × 10^{-3} M in benzoic acid.

t (min)	0	15	33	55	84	117	172
R	0.430	0.350	0.280	0.210	0.150	0.110	0.055

$k_{inv} = 102 \times 10^{-6}$ sec^{-1}

t (min)	0	24	48	90	144	210
D	480.8	416.1	357.3	282.0	204.4	138.9

$k_{ex} = 101 \times 10^{-6}$ sec^{-1}

(ii) 0.4431 g silane in 35.20 g solution 0.95 × 10^{-3} M in benzoic acid.

t (min)	0	13	36	56	81	126	166
R	0.410	0.360	0.270	0.220	0.170	0.115	0.075

$k_{inv} = 878 \times 10^{-7}$ sec^{-1}

t (min)	0	24	48	90	150	210
D	472.4	429.5	380.7	304.6	209.7	156.6

$k_{ex} = 900 \times 10^{-7}$ sec^{-1}

Sodium acetate solution

(i) 0.5934 g silane in 50 ml solution 1.45 × 10^{-3} M in sodium acetate.

t (h)	0	3.0	8.0	13.0	24.0	30.0	36.0
R	0.330	0.285	0.230	0.180	0.105	0.080	0.050

$k_{inv} = 66.0 \times 10^{-7}$ sec^{-1}

t (h)	0	5.05	11.0	23.65	32.35	47.65
D	124.7	105.7	93.2	70.1	57.4	42.8

$k_{ex} = 64.5 \times 10^{-7}$ sec^{-1}

(ii) 0.5291 g silane in 34.05 g solution 1.13 × 10^{-3} M in sodium acetate.

t (h)	0	3.25	6.60	8.75	11.55	22.70	26.50	29.25	33.30
R	0.480	0.360	0.290	0.260	0.220	0.120	0.095	0.080	0.060

$k_{inv} = 85.2 \times 10^{-7}$ sec^{-1}

t (h)	0	5.85	11.45	23.55	31.75	47.15
D	463.2	369.8	314.5	220.2	171.7	114.3

$k_{ex} = 84.6 \times 10^{-7}$ sec^{-1}

Sodium methoxide solution

(i) 0.4195 g silane in 38.05 g solution 4.0 × 10^{-5} M in sodium methoxide.

t (min)	0	32	83	157	228	339	565
R	0.370	0.300	0.230	0.170	0.130	0.105	0.055

t (min)	0	43	104	189	258	337	567
D	186.6	166.0	146.5	123.5	115.9	100.5	81.3

(ii) 0.4175 g silane in 36.15 g solution 6.2 × 10^{-5} M in sodium methoxide.

t (min)	0	23	42	63	90
R	0.320	0.205	0.125	0.085	0.055

t (min)	0	20	40	60	84	157	304
D	174.5	136.6	110.5	89.1	70.3	40.7	17.5

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SUMMARY

The stereochemistry of the methoxyl exchange between a methoxysilane and methanol (either alone or containing acid or base catalysts) has been investigated using optically active methoxymethyl-α-naphthylphenylsilane containing tritium in the methoxyl group. For any set of conditions the rate of methoxyl exchange is equal to half the rate of racemization, so that inversion of configuration at silicon must accompany every act of substitution.

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