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THE NATURE AND CONSEQUENCES OF THE INTERACTION OF PHOSPHORYL NUCLEOPHILES WITH A TRIORGANOSILYL CHLORIDE

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Summary

In order to throw light on the possible role of positively charged tetra-coordinate silicon intermediates in the racemization of α-NpPhMeSiCl (**1**) induced by uncharged nucleophiles two sets of kinetic studies have been carried out. In the first the rates of two reactions namely racemization of **1** catalysed by $(PhO)_2(Me_3SiO)P{=}O$ (**2**) and transsilylation of **2** with **1**, which take place together and are believed to involve the same intermediate were determined; the transsilylation was found to be faster than the racemization, and involved transient formation of an optically active product. In the second the racemization of **1** catalysed by HMPT in various CCl_4/CH_2Cl_2 mixtures was studied; the rate was found to increase markedly with increase in the dielectric constant of the medium. The results of both sets of experiments were consistent with a mechanism involving a silyloxyphosphonium cation intermediate.

Introduction

Nucleophilic catalysis by uncharged nucleophiles such as HMPT plays an important role in some reactions at a silicon centre. This catalysis was clearly demonstrated by Corriu and his coworkers for racemizations of triorganohalosilanes [1–4]. Two mechanisms for the catalysis were initially proposed (Scheme 1), the first involving the hexacoordinate silicon intermediate I and the second the pentacoordinate silicon cationic intermediate II. Later, we pointed out that a process involving ionization with the formation of the tetracoordinate silicon cation intermediate III (Scheme 1) must also be taken into account [5].

It is reasonable to assume that different systems may involve different reactions routes from Scheme 1. The case of the racemization of triorganosilyl chlorides has given rise to some controversy. We suggested it might proceed via route III [5], but the results of extensive studies on various triorganosilyl chloride-nucleophile systems and comparison with the behaviour of analogous systems involving germanium, tin,

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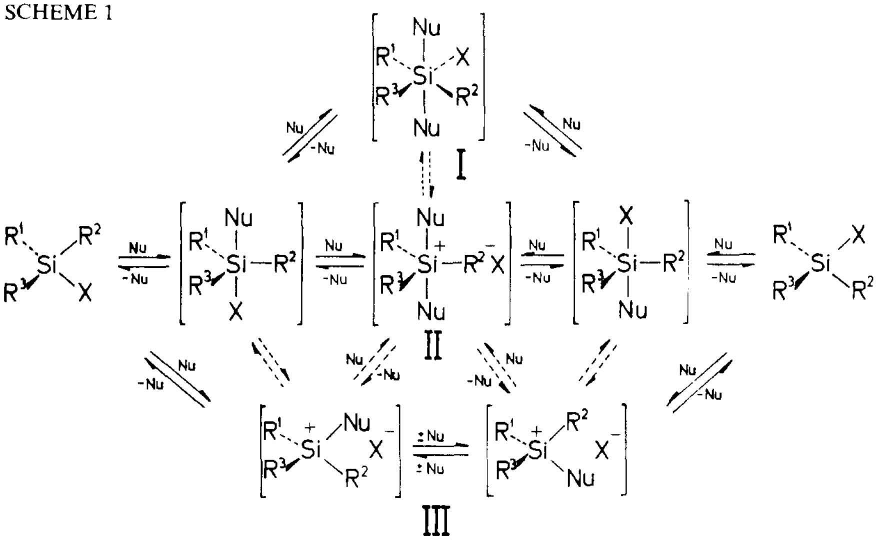
SCHEME 1



and phosphorus led Corriu, Dabosi, and Martineau [6] to conclude that the formation of the intermediate III was very unlikely. Nevertheless, we must point out that all three mechanisms of Scheme 1 are kinetically equivalent only and it is possible that the intermediate III is present at a very low concentration which still is kinetically significant. Recently the mechanism III received some support from studies of the interaction of triorganosilyl halides with DMF [7] and of the amine-catalysed alcoholysis of some chlorosilanes [8].

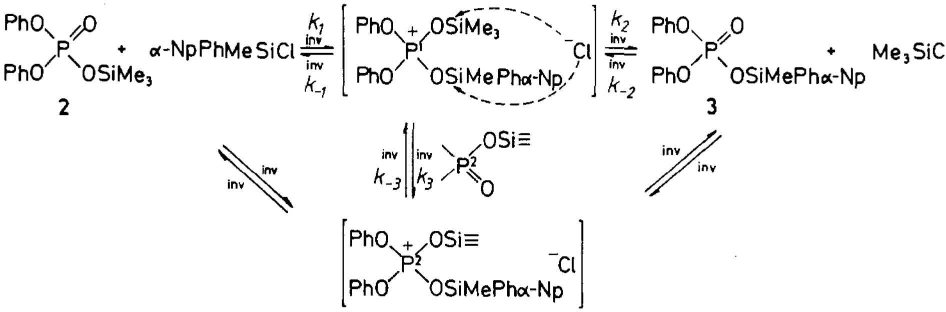
We have explored two ways of confirming the existence of mechanism III in the racemization of triorganosilyl chlorides. The first involved a search for a correlation between the rate of the silyl chloride racemization and that of the disappearance of the phosphoryl nucleophile, both processes resulting from the same interaction between the nucleophile and the silyl chloride. The second was the study of the effect of dielectric constant on the HMPT-induced racemization of an triorganosilyl chloride. We reasoned that experiments could provide evidence for rejection of mechanism III (or at least cast serious doubt upon it) even if they could not unambiguously confirm its existence.

The rate correlation experiments

Interaction of the phosphoryl nucleophile with trialkylhalosilane is known not only to lead to racemization at the silicon centre but also to involve important changes in the phosphorus moiety. A good example is the replacement of ester alkyl groups by silyl groups, which is often used in synthesis of acids of phosphorus via their silyl esters [9–12]. The mechanism of this reaction involves analogous phosphonium intermediates to those which appear in reaction pathway III of the racemization scheme [13]. By proper choice of a phosphorus nucleophile it is thus possible to observe together both the racemization and the reaction at the phosphorus centre. If the phosphonium intermediate mechanism is valid then the intermediate should be common for both these competitive processes. This in turn should have consequences for the relative rates of the two processes which should permit verification of the mechanism.

The phosphoryl nucleophile chosen for the racemization of optically active α-NpPhMeSiCl was trimethylsilyldiphenyl phosphate (**2**). If the reaction involves the intermediate III then the phosphonium cation must have two silyl groups equivalently bound to the phosphorus centre, both exposed to nucleophilic attack by the counter-ion (Scheme 2), and so exchange of silyl groups between the halide and the phosphorus ester (transsilylation) should take place [14].

SCHEME 2



Furthermore the third order kinetics of the racemization [3] means that the first step, the phosphonium salt formation, should be faster than the second, the attack of another phosphate molecule at the chiral silicon in the phosphonium intermediate, i.e. $k_{-1} \gg k_3$[=P(O)OSi≡]. The transsilylation is thus expected to be faster than the racemization, since the decomposition of the intermediate to the transsilylation product is unlikely to be much slower than the decomposition to the substrate; if this is the case, then the transsilylation should lead to formation of optically active ester.

Reactions in the system (−)-α-NpPhMeSiCl + $(PhO)_2P(O)OSiMe_3$ were followed by ^{31}P NMR spectroscopy and by changes in the optical rotation. The results are reported below.

The transsilylation reaction

(1) The transesterification reaction (Scheme 2) in CCl_4 occurs readily at room temperature and may be conveniently studied by ^{31}P NMR spectroscopy by monitoring the changes in the heights of the signals at δ −20.8 ppm for ester **2** and δ −21.3 ppm for ester **3**.

(2) The reaction kinetics correspond to a second order reaction (first order in both the ester and the silyl chloride) proceeding to equilibrium.

(3) Since analysis by ^{31}P NMR is liable to significant error, the rate was measured over a wide temperature range, −10 to 35°C. Values at 35°C of the rate constant, the equilibrium constant, and the activation parameters were: $k_{ex}(35°)$ 0.050 $mol^{-1}\,dm^3\,s^{-1}$, K (35°) = 1.5, $\Delta H^{\ddagger} = 5.0$ kcal mol^{-1}, $\Delta S^{\ddagger} = -39$ cal mol^{-1} deg^{-1}.

The reaction shows similar features, i.e. a low activation energy and a high negative activation entropy, to those of the racemization of chlorosilane by uncharged nucleophiles [4]. This argues in favour for a common intermediate for the two processes.

The racemization

The optical rotation-time curve corresponded to a first order process, and gave a direct indication of the rate of racemization catalysed by **2** only at low ester to silane ratios. At relatively high concentrations of the ester the initial portion of the curve deviated from first order, and this deviation became larger and extended over a larger portion of the curve upon increase of the catalyst to substrate ratio. The period over which the deviation occurred, corresponded well to the time to reach the equilibrium position of the transsilylation (Fig. 1). This observation may be accounted for by assuming that the transsilylation is faster than the racemization and proceeds stereoselectively, giving initially an optically active α-naphthylphenylmethylsilyl ester.

The ratio of relevant specific rates for the transsilylation and the racemization in the system involving **1** and **2** was about 5/1.

The rates of the racemization of the optically active **1** were also determined with two other esters as catalysts namely racemic α-NpPhMeSiOP(O)(OPh$_2$) (**3**) and MeOP(O)(OPh)$_2$ (**4**). The catalytic activity of **3** was comparable to that of **2** (the rates differ by about a factor of 2), but both of these esters showed much higher catalytic activities than the methyl ester **4**. The racemization catalysed by the latter was about two order of magnitudes lower at corresponding initial concentrations. This indicates a fundamental difference between the mechanisms of catalysis of the racemization by the silyl and by the alkyl esters. Only for the latter can the mechanism of Scheme 1 be considered. In the case of the silyl ester nucleophiles the chiral silyl chloride is first stereoselectively transformed to the chiral silyl phosphate,

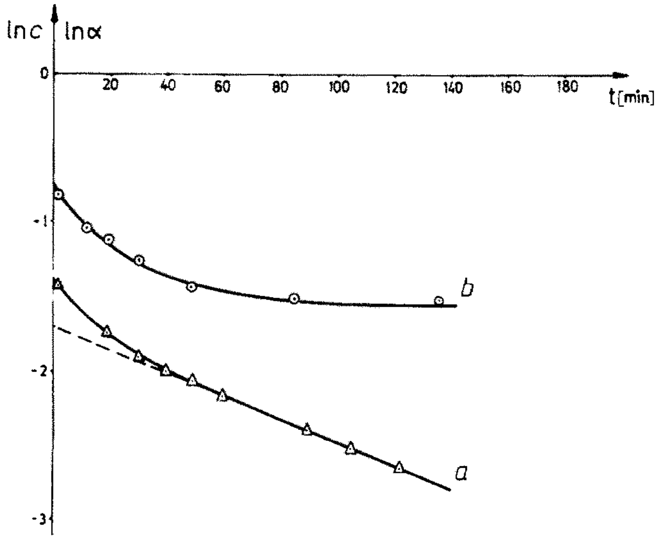
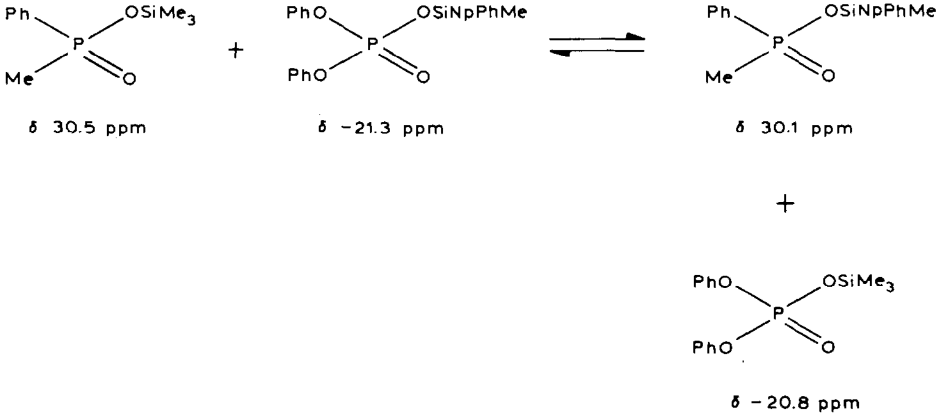


Fig. 1. Comparison of the optical rotation-time curve (a) for the racemization of (−)-α-NpPhMeSiCl (**1**) catalysed by (PhO)$_2$P(O)(OSiMe$_3$) (**2**) with the conversion-time curve (b) for the transsilylation of **2** by **1** in the same system. Solvent CCl$_4$; temperature 35°C; initial concentrations: [**1**] 0.25 mol dm^{-3}, [**2**] 0.25 mol dm^{-3}. The specific rates calculated as the second order rate constants, were: k_{rac} 1.9×10^{-4} dm^3 mol^{-1} s^{-1}, $k_{exch.}$ 10×10^{-4} dm^3 mol^{-1} s^{-1}.

which undergoes subsequent racemization by another route. The rate of the racemization according to Scheme 2 must be lower, probably comparable to the rate of the racemization induced by **4**. Thus it must be also distinctly lower than the rate of the transsilylation $k_2 \gg k_3[{=}P(O)OSiMe_3]$, and this is in keeping with the formation of the phosphonium ion intermediate in the system.

We suggest that the racemization of the optically active silyl ester **3** may result from intermolecular silyl group migration, which was shown to occur by mixing two esters having structures differing in of both the phosphorus and the silicon moieties. After some minutes two additional signals appeared in the ^{31}P NMR spectrum, indicating the occurrence of exchange according to the following scheme:



The reaction is presumably catalysed by traces of acids which are formed in the system, and this would account for the rather poor reproducibility of the rate of change in optical rotations.

Effect of dielectric constant on the racemization of α-NpPhMeSiCl

It was thought possible that examination of the effect of the polarity of the medium, on the rate of nucleophile-induced racemization of a triorganosilyl chloride might allow a choice to be made between the mechanism involving the intermediate I and mechanisms involving II and III. These last processes involve the ionization of a silicon–chloride bond, and so the transition states should be distinctly more polar than the initial state, and a considerable increase of the reaction rate with increasing dielectric constant of the medium would be expected. Absence of such an effect would strongly favour intermediate I, the formation of which does not involve a strongly polar transition state.

There were no data which permitted evaluation of the effect of the dielectric constant on this process. There have been comparisons of the rates of the racemization of chlorosilanes in various solvents and in mixed solvents [4,15,16], but the results are not conclusive because the dielectric constant effect cannot be separated from the effect of specific interaction with the solvent. Our approach was to study the rate of the HMPT induced racemization of (−)-α-NpPhMeSiCl (**1**) in various mixtures of carbon tetrachloride and methylene chloride. The carbon tetrachloride is inert towards **1** and the spontaneous racemization in methylene chloride occurs so slowly that it is negligible compared with the HMPT-catalysed process. Both these

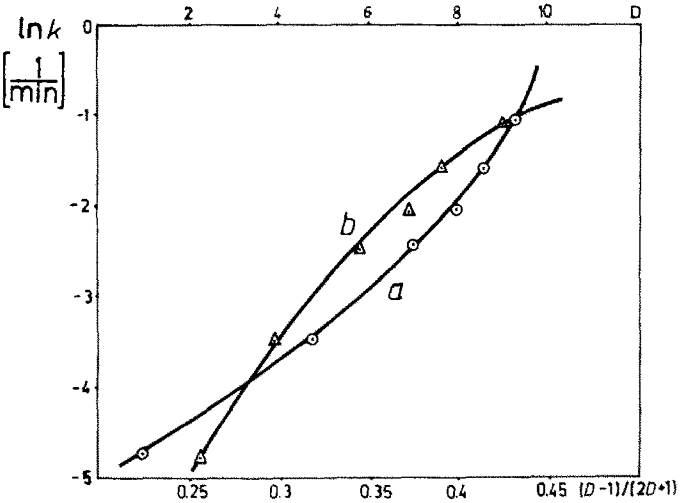


Fig. 2. Dependence of the rate of racemization of (−)-α-NpPhMeSiCl catalysed by HMPT in CH_2Cl_2/CCl_4 mixtures on the dielectric constant of the system. Temperature 25°C, [HMPT] 25×10^{-3} mol dm^{-3}, $[(-)\text{-}\alpha\text{-NpPhMeSiCl}]_0$ 0.2 mol dm^{-3}; (a) ln k_{rac} vs D, (b) ln k_{rac} vs $\frac{D-1}{2D+1}$.

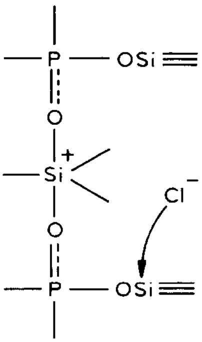
solvents have very low nucleophilicity, and so the differences in the specific rate in various CH_2Cl_2/CCl_4 mixtures must be almost entirely due to the dielectric constant effect.

The results shown in Fig. 2, reveal a pronounced susceptibility of the reaction to changes with polarity of the medium. The observed dependence did not conform to the Kirkwood equation, but that is quite usual for reactions studied in media of relatively low dielectric constant.

The result is consistent with the ionization mechanisms II and III.

Concluding remarks

The correlations between the rates of the racemization and the transsilylation and the dependence of the rate of racemization on the dielectric constant can both be understood in terms of the mechanism involving a tetra-coordinate silicon intermediate. There is no need to assume the formation of an expanded octet intermediate, although participation of such a species cannot be excluded. Route I seems to us to be improbable in the light of the observed dielectric constant effect; an important requirement for the formation of a hexacoordinate silicon acyclic compound seems to be small bulk and strongly electron-withdrawing character of the substituents and these conditions are not met in the present case. The choice is thus between route II and III. The rate correlation results cannot be used to test the existence of the expanded octet intermediate mechanism since it is not necessary that the intermediate II should undergo conversion in the direction of the transsilylation, and it might disappear by another route. It is noteworthy that if the transsilylation went through the intermediate II it would involve preferential attack of the chloride ion on a tetra-coordinate silicon rather than on a penta-coordinate silicon centre, which would conflict with the concept of "extra-reactivity" of hyper-valent centres.



Thus we prefer mechanism III, since it accounts consistently for the two reactions, the reaction of the chlorosilane and the transformation of the nucleophile.

Experimental

Solvents and reagents

The CCl_4 was distilled from P_2O_5, CH_2Cl_2 from $LiAlH_4$, and hexane from CaH_2.

Me_3SiCl and Me_3SiBr were purified by distillation, racemic α-NpPhMeSiCl and $(-)$-α-NpPhMeSiCl, $[\alpha]_D$ $-6.3°$ were made as previously described [17].

HMPT (Merck) was distilled from CaH_2 under reduced pressure. $(PhO)_2P(O)OMe$ was made by methanolysis of (PhO)P(O)Cl with Et_3N as HCl acceptor and was purified by vacuum distillation. PhMeP(O)OMe was obtained by the Arbuzov reaction from $PhP(OMe)_2$ and MeI and distilled under vacuum.

Synthesis of diphenyl(trimethylsilyl)phosphate (2) and trimethylsilyl phenylmethylphosphinate (6)

The phosphate **2** was obtained in 85% yield from $(PhO)_2P(O)OMe$ and Me_3SiBr by the procedure described in ref. 12; and it had b.p. 140–145°C/0.5 mmHg; $\delta(^{31}P)$ -20.8 ppm.

The phosphinate **6** was obtained analogously in 70% yield from PhMeP(O)OMe and Me_3SiBr, it had b.p. 105–110°C/0.35 mmHg. $\delta(^{31}P)$ 30.5 ppm.

Synthesis of diphenyl(α-naphthylphenylmethylsilyl)phosphate (3) and α-naphthylphenylmethylsilyl phenylmethylphosphinate 7

Solutions of equimolar amounts of **2** and **1**-racemic, both in CCl_4 (1/1 v/v), were mixed. The solvent and Me_3SiCl were distilled off and the residue was heated on high vacuum line (60°C/0.01 mmHg, 5 h) as Me_3SiCl was collected in a vacuum trap. The ^{31}P NMR spectrum showed only one signal $\delta(^{31}P)$ -21.2 ppm. The product, which was formed in 100% yield was a viscous liquid, and was purified by molecular distillation.

The phosphinate **7** was made analogously from **6** and *o*-racemic **1**, the yield (by ^{31}P NMR) was 100% $\delta(^{31}P)$ 30.1 ppm.

Kinetics of the transsilylation

The reaction between racemic α-NpPhMeSiCl (**1**) and $(PhO)_2P(O)OSiMe_3$ (**2**) was monitored by ^{31}P NMR using a Bruker AX90 FT spectrometer. The spectra were recorded locked on external deuterated acetone or deuterated DMSO. The heights of the signals from **2** and the product **3** were directly compared. All operations were carried out under dry nitrogen. The CCl_4 solutions of **1** and **2** were subsequently introduced into a 5 mm o.d. NMR tube from a Hamilton syringe. The tube was tightly sealed.

Kinetics of racemization

The racemization of $(-)$-α-NpPhMeSiCl (**1**) in CCl_4 catalysed by **4**, **7** or $(PhO)_2P(O)OMe$, and the racemization of **1** in CH_2Cl_2/CCl_4 system catalysed by HMPT were monitored by use of a Perkin–Elmer 241 MC photopolarimeter fitted with a water jacket thermostatted 10 cm cell. The cell was carefully purged with purified nitrogen and tightly closed. All operations involving the substrate and catalysts were carried out in such a way as to avoid contact with atmosphere. The directly compared transsilylations and racemizations were carried out in the same solution.

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