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The reaction of isosteric isobutyl(isopropoxy)silanes $^{i}Bu_n(^{i}PrO)_{3-n}SiH$ (n = 0–3) with allyl bromide in the presence of platinum compounds

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Abstract

The isosteric silanes $^{i}Bu_n(^{i}PrO)_{3-n}SiH$ react with allyl bromide to yield the corresponding bromides $^{i}Bu_n(^{i}PrO)_{3-n}SiBr$. The reactivities of the silanes fall in the sequence: $^{i}Bu(^{i}PrO)_2SiH \geq {}^{i}Bu_2(^{i}PrO)SiH > (^{i}PrO)_3SiH > {}^{i}Bu_3SiH$, which can be accounted for in terms of the anomeric effects at the silicon atom.

Introduction

It is known that hydrosilylation of allyl chloride is accompanied by formation of propylene [1,2]. The yield of propylene depends upon the structure of the catalyst and to some extent upon the structure of silane [2]. Allyl and methallyl chlorides undergo hydrosilylation by deuterated trichlorosilane, Cl_3SiD, to give 3-chloropropyl(trichlorosilane)-2-D_1 or 3-chloro, 2-methylpropyl(trichlorosilane)-2-D_1. The side reaction, propylene formation, occurs only for allyl chloride, yielding propylene-3-D_1. The formation of propylene from β-chloroisopropyltrichlorosilane via β-elimination seems very unlikely since this silane is stable under hydrosilylation conditions [3]. Chloro- and dichlorobutenes react with CH_3Cl_2SiH in a complex way and rapid migration of the double bond is observed [3]. Some propylene formation was observed in the hydrosilylation of allyl bromide and allyl acetate with methyldichlorosilane and 1,1,3,3,3-tetramethyldisiloxane [4].

Structure–reactivity relationships for the isosteric silanes $Pr_n(EtO)_{3-n}SiH$ were the subject of investigation some years ago [5,6]; in both hydrosilylation of 1-hexene in the presence of H_2PtCl_6 [5] and in alkaline solvolysis [6] $Pr(EtO)_2SiH$ was the most reactive. The results were partly explained in terms of variation in the extent of p_π-d_π conjugation [5,6].

We have investigated the alcoholysis of isosteric silanethiols $^{i}Bu_n(^{i}PrO)_{3-n}SiSH$, and under some conditions $^{i}Bu(^{i}PrO)_2SiSH$ has proved to be the most reactive [7]. Subsequently we observed that the isosteric silanes $^{i}Bu_n(^{i}PrO)_{3-n}SiH$ react with

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allyl bromide to yield the corresponding bromosilanes and propylene almost exclusively [8,9]. It seemed to us of interest to find out whether there are some similarities in the variation in reactivity in these two closely related sets of compounds and whether enhanced reactivity of compounds with two alkoxy groups is a general feature of organosilicon compounds.

Table 1

Pseudo-first order rate constants, k, for reaction of $^i\text{Bu}_n(^i\text{PrO})_{3-n}\text{SiH}$ or $(p\text{-XC}_6\text{H}_4)_3\text{SiH}$ with allyl bromide in the presence of H_2PtCl_6 or $Pt(PPh_3)_2(C_2H_4)$ as catalyst. ($T = 75 \mp 1°$ C; initial silane concentration 0.4 M; k: calculated from the relationships ln c_{silan} vs. time; r: correlation coefficient; n: number of measurement points)

No.	Silane	Catalyst conc. $\times 10^5$ (mol l^{-1})	$k \times 10^4$ (min^{-1})	$r(n)$
1a	$(^i\text{PrO})_3\text{SiH}$	15 [a]	31	0.9983(10)
1b	$(^i\text{PrO})_3\text{SiH}$	30 [a]	80	0.9556(8)
1c	$(^i\text{PrO})_3\text{SiH}$	60 [a]	160	0.9956(6)
2a	$^i\text{Bu}(^i\text{PrO})_2\text{SiH}$	3 [a]	105	0.9917(9)
2b	$^i\text{Bu}(^i\text{PrO})_2\text{SiH}$	6 [a]	220	0.9911(8)
2c	$^i\text{Bu}(^i\text{PrO})_2\text{SiH}$	6 [a]	320	0.9939(7)
2d	$^i\text{Bu}(^i\text{PrO})_2\text{SiH}$	15 [a]	430	0.9957(9)
2e	$^i\text{Bu}(^i\text{PrO})_2\text{SiH}$	30 [a]	780	0.9853(6)
3a	$^i\text{Bu}_2(^i\text{PrO})\text{SiH}$	6 [a]	135	0.9999(4)
3b	$^i\text{Bu}_2(^i\text{PrO})\text{SiH}$	6 [a]	230	0.9900(7)
3c	$^i\text{Bu}_2(^i\text{PrO})\text{SiH}$	15 [a]	420	0.9973(5)
3d	$^i\text{Bu}_2(^i\text{PrO})\text{SiH}$	30 [a]	590	0.9951(6)
3e	$^i\text{Bu}_2(^i\text{PrO})\text{SiH}$	60 [a]	1430	0.9996(4)
3f	$^i\text{Bu}_2(^i\text{PrO})\text{SiH}$	60 [a]	1500	0.9992(4)
4a	$^i\text{Bu}_3\text{SiH}$	15 [a]	30	0.9832(8)
4b	$^i\text{Bu}_3\text{SiH}$	15 [a]	19	0.9935(9)
4c	$^i\text{Bu}_3\text{SiH}$	30 [a]	33	0.9621(9)
4d	$^i\text{Bu}_3\text{SiH}$	60 [a]	120	0.9934(6)
5a	Ph_3SiH	6 [a]	50	0.9674(9)
5b	Ph_3SiH	15 [a]	160	0.9731(7)
5c	Ph_3SiH	4.8 [b]	16	0.8995(5)
5d	Ph_3SiH	9.6 [b]	50	0.9857(6)
5e	Ph_3SiH	19.2 [b]	80	0.9844(7)
5f	Ph_3SiH	38.4 [b]	170	0.9921(4)
5g	Ph_3SiH	38.4 [b]	160	0.9972(6)
5h	Ph_3SiD	38.4 [b]	108	0.9791(7)
5i	Ph_3SiD	38.4 [b]	101	0.9800(5)
5j	Ph_3SiH	38.4 [c]	6	0.8810(5)
6a	$(p\text{-MeC}_6\text{H}_4)_3\text{SiH}$	6 [a]	130	0.9597(6)
6b	$(p\text{-MeC}_6\text{H}_4)_3\text{SiH}$	15 [a]	650	0.9959(6)
7a	$(p\text{-ClC}_6\text{H}_4)_3\text{SiH}$	6 [a]	160	0.9427(5)
7b	$(p\text{-ClC}_6\text{H}_4)_3\text{SiH}$	15 [a]	840	0.9827(5)
8a	$(p\text{-MeOC}_6\text{H}_4)_3\text{SiH}$	6 [a]	710	0.9010(4)

[a] H_2PtCl_6 as catalyst. [b] $Pt(PPh_3)_2(C_2H_4)$ as catalyst. [c] $Pt(PPh_3)_2(C_2H_4)$ in the presence of 0.035 M PPh_3.

Results and discussion

The isosteric silanes $^{i}Bu_n(^{i}PrO)_{3-n}SiH$ react with allyl bromide almost exclusively according to eq. 1.

$$^{i}Bu_n(^{i}PrO)_{3-n}SiH + C_3H_5Br \xrightarrow{cat} {}^{i}Bu_n(^{i}PrO)_{3-n}SiBr + C_3H_6 \qquad (1)$$

The reactions were carried out with excess of allyl bromide. The pseudo-first-order rate constants with various H_2PtCl_6 and $Pt(Ph_3P)_2(C_2H_4)$ concentrations for the reactions of $^{i}Bu_n(^{i}PrO)_{3-n}SiH$ and the *p*-substituted silanes $(p\text{-}XC_6H_4)_3SiH$ are given in Table 1.

In all cases the best fit was obtained for first-order kinetics. The rate constants at low concentration of catalyst are not always satisfactorily reproducible, so that the exact determination of the reaction order in respect to catalyst is difficult, but it seems to be close to one.

In Table 2 are listed the concentrations of silane $^{i}Bu_n(^{i}PrO)_{3-n}SiH$ after given reaction times in the presence of the very efficient Pt^0 hydrosilylation catalyst $Pt(Ph_3P)_2(C_2H_4)$ at room temperature.

The reaction shows interesting features, in some cases different from those for the hydrosilylation route:

1. The investigated reaction is first order in respect to silane, while hydrosilylation is mainly zero order [10,12]. The order with respect to the catalyst seems to be ca. one;
2. The reaction is not very sensitive to steric effects at the silicon atom, and some silanes which do not react by hydrosilylation route, probably because of steric hindrance, are readily brominated (for example, Ph_3SiH). Furthermore Et_3SiH yields only Et_3SiBr, although with styrene it reacts by hydrosilylation [10];
3. The reactivities of the isosteric silanes in bromination falls in the following sequence: $^{i}Bu(^{i}PrO)_2SiH \geq {}^{i}Bu_2(^{i}PrO)SiH > (^{i}PrO)_3SiH > {}^{i}Bu_3SiH$. This sequence is almost the same as that for nucleophile-catalysed alcoholysis of isosteric silanethiols $^{i}Bu_n(^{i}PrO)_{3-n}SiSH$ in acetonitrile [7];
4. The reaction shows a deuterium kinetic isotope effect of ~ 1.7, and the reaction is strongly inhibited by the presence of Ph_3P (Table 1, 5j);
5. Electron releasing substituents in the aromatic ring increase the rate in bromination of *para* substituted triarylsilanes (Table 1, No. 5–8). The same is true for some hydrosilylation reactions [10] and for bromination of silanes by molecular bromine [14];

Table 2

The reactions of $^{i}Bu_n(^{i}PrO)_{3-n}SiH$ with allyl bromide in the presence of $Pt(Ph_3P)_2(C_2H_4)$ as catalyst. ($T = 25\,°C$; $c_{cat} = 0.0003\ M$; initial concentration of C_3H_5Br 5.25 M)

Reaction time (h)	$(^{i}PrO)_3SiH$ M	$^{i}Bu(^{i}PrO)_2SiH$ M	$^{i}Bu_2(^{i}PrO)SiH$ M	$^{i}Bu_3SiH$ M
0	2.17	2.17	2.17	2.17
63	1.93	1.82	1.64	2.17
145	-	1.06	1.25	-
233	1.35	0.31	0.27	2.10

6. Use of the Pt^0 complex $Pt(Ph_3P)_2(C_2H_4)$ as catalyst results in the same products and does not change the reactivity sequence for the silanes $^iBu_n(^iPrO)_{3-n}SiH$. No products of hydrosilylation were found from the reaction at 25 or at 75°C

Conclusions

It seems very unlikely that production of propylene involves formation of $CH_3CH(SiR_3)CH_2Br$ followed by β-elimination [3].

In view of available information about the mechanism of hydrosilylation [10–13] and of the observed first-order kinetics with respect to the silane and probably first-order in respect to the catalyst a simple route can be suggested (eq. 2).

$$\underset{\text{(I)}}{R_3SiH + Pt[L]_m} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \underset{\text{(II)}}{R_3SiPt(H)[L]_n} \xrightarrow{k_2,\ C_3H_5Br} R_3SiBr + Pt[L]_m + C_3H_6 \qquad (2)$$

Two possibilities would give rise to the observed first-order in silane and catalyst if a steady-state approximation is made:

a. $k_{-1} \neq 0$, implying that k_1, k_{-1} and k_2 determine the reaction rate;

b. $k_{-1} \sim 0$, implying that k_1 is the rate limiting step.

I denotes the actual catalyst formed from H_2PtCl_6 or $Pt(Ph_3P)_2(C_2H_4)$ in the presence of allyl bromide and silane. We assume that it is a Pt^0 complex (see below) in which allyl bromide is bonded to Pt. This assumption is consistent with the strong retarding effect of Ph_3P on the reaction.

Recent investigations show that in terms of the route depicted in eq. 2, possibility a (i.e. $k_{-1} \neq 0$) is more probable, because the oxidative addition of R_3SiH to Pt^0 complexes is known to be facile and reversible [10]. This implies that the rearrangement within the catalyst complex II must be irreversible slow step. It may be preceeded by some reversible steps but we do not have sufficient information to discuss that. The symbol k_2 in eq. 2 represents the overall rate constant for what may be a multistep process.

Electron-releasing substituents on the phenyl ring enhance the overall reaction rate for triarylsilanes. This electronic effect may affect the k_1/k_{-1} ratio, but it will essentially favour a reaction in which H^- and/or Br^- migrate. On the basis of the value of the deuterium kinetic isotope effect (ca. 1.7) for Ph_3SiD we conclude that there is some Pt–H bond breaking in the rate limiting step but the smallness of this effect strongly suggests that the rate limiting step may be irreversible Br^- migration. The bromine migration is facilitated by the π-acceptor properties of allyl bromide and the of σ-donor properties of R_3Si group.

The influence of alkoxy substituents on silicon atom on the reactivity of isosteric silanes $^iBu_n(^iPrO)_{3-n}SiH$ can be best explained in terms of their anomeric and polar effects.

The anomeric effect can efficiently operate only in a molecule where the central atom (here Si) is surrounded by at least one heteroatom with a one or more electron pairs (here O) and one atom X more electronegative than the central atom (here O, C, H). In the localized orbitals picture the anomeric effect is attributed to the interaction of the lone pair orbital of heteroatom, here $p_\pi(O)$, with the geminal $\sigma^*(Si{-}X)$ antibonding orbital. The $\sigma^*(Si{-}X)$ orbital is expected to be lower in energy the higher the electronegativity of X. The overlap $p_\pi(O)$ with $\sigma^*(Si{-}X)$ will be larger when X is more electronegative owing to the greater polarization towards silicon of σ^*(Si–X). Thus the energy of the anomeric interaction falls in the following sequence:

$$p_\pi(\mathrm{O}) \rightarrow \sigma^*(\mathrm{Si{-}O}),\ p_\pi(\mathrm{O}) \rightarrow \sigma^*(\mathrm{Si{-}C}),\ p_\pi(\mathrm{O}) \rightarrow \sigma^*(\mathrm{Si{-}H}).$$

For more detailed discussions see refs. 15–17.

The anomeric effect manifests itself in the energies, geometries (usually a *gauche* conformation is adopted), weakening of the Si–X bond, and increase in the rotation barriers around the Si–O bond.

We now consider the influence of polar and anomeric effects of alkoxy groups on the reactivities of the four isosteric silanes.

(a) $^i\mathrm{Bu}_3\mathrm{SiH}$. As noted above, electron-withdrawing substituents lower the reaction rate and so the rate should be greater then those of the alkoxy-substituted compounds. No anomeric effect operates, which means that there is neither any increased antibonding character of the Si–H bond or an additional rotation barrier around the Si–O bond. The steric hindrance is highest in this case because the rotations of all three ^{i}Bu groups are not inhibited, and thus steric reasons must be responsible for the fact that this compound is the least reactive.

(b) $^i\mathrm{Bu}_2(^i\mathrm{PrO})\mathrm{SiH}$. The electron-withdrawing effect of one ^{i}PrO group should lower the reaction rate compared with that for $^i\mathrm{Bu}_3\mathrm{SiH}$. However, the anomeric effect can operate. The p_π electron pair of O takes up a position mainly antiperiplanar to the adjacent Si–C bond (C is more electronegative than H). The additional rotation barrier around the Si–O axis will be not high, but the decreased steric demand of the $^i\mathrm{Bu}_2(^i\mathrm{PrO})\mathrm{Si}$ group more than compensates for the unfavourable polar effect, and thus the reactivity of this silane is higher than $^i\mathrm{Bu}_3\mathrm{SiH}$.

(c) $^i\mathrm{Bu}(^i\mathrm{PrO})_2\mathrm{SiH}$. In terms of electronic effects the presence of two electronegative groups should make this less reactive than $^i\mathrm{Bu}_2(^i\mathrm{PrO})\mathrm{SiH}$. However, the anomeric effect is important in determining the conformation of this compound [15]. Owing to strong mutual $p_\pi(\mathrm{O}) \rightarrow \sigma^*(\mathrm{Si{-}O})$ interactions there are two favourable conformers, equivalent in respect of the anomeric effect, with C_s and C_2 symmetry (*g*, *g*-conformer) respectively. The second conformer should be the more stable because of through-space dipole-dipole interactions [16]. The additional rotational barrier around the Si–O axis should be high, since there is only one favourable position during the rotation around the Si–O bond and this partially inhibits rotation of two ^{i}PrO groups and therefore the effective steric demand of the $^i\mathrm{Bu}(^i\mathrm{PrO})_2\mathrm{Si}$ system should be smaller. This steric influence, in spite of the electronic effect of two ^{i}PrO groups, lead to higher reactivity for $^i\mathrm{Bu}(^i\mathrm{PrO})_2\mathrm{SiH}$.

(d) $(^i\mathrm{PrO})_3\mathrm{SiH}$. The electronic effect is very unfavourable in this case. The most stable propellane structure [16] of C_3 symmetry allows anomeric interaction between all the oxygen atoms but the rotation around the Si–O axis will be relatively unhindered since there are four favourable positions with respect to anomeric interaction and two unfavourable ones during complete rotation around the Si–O axis on the assumption that the two other ^{i}PrO groups are fixed. The steric demand of the $(^i\mathrm{PrO})_3\mathrm{Si}$ should be greater than of the $^i\mathrm{Bu}(^i\mathrm{PrO})_2\mathrm{Si}$ group. These two factors, electronic and steric, acting together, are responsible for the low reactivity of this compound.

We conclude that the observed reactivity trend reflects the combined effect of the electron-withdrawing influence of the alkoxy groups and the steric effect arising from hindered rotation of these groups as a result of the anomeric effect. The sequence is not determined by weakening of the Si–H bond. The conformations with p_{π}(O) electron pair antiperiplanar to the Si–H bond are not favourable in our series. It is noteworthy that the additional rotation barrier is not high compared with that for an actual double bond, but in cases where a reaction is not very sensitive to polar effects but is very sensitive to steric effects such anomeric interactions can be critical.

Experimental

Commercial (Merck) $H_2PtCl_6 \cdot 6H_2O$ was dissolved in isopropanol and the solution diluted with allyl bromide to give a stock solution. $Pt(Ph_3P)_2(C_2H_4)$ was dissolved in allyl bromide. The reaction mixtures were placed under argon in 5 ml vessels closed with a polyurethane membrane and kept at 75 ± 1° C in a glycol bath. The experimental data are listed in Table 1. Some reactions in the presence of $Pt(Ph_3P)_2(C_2H_4)$ were carried out at 25° C (Table 2). The rates of the brominations were determined by monitoring the disappearance of the silane peaks in GC. GC analysis revealed that the corresponding bromosilanes has been formed in nearly quantitative yield. In case of $^{i}Bu_2(^{i}PrO)SiH$ in the presence of $Pt(Ph_3P)_2(C_2H_4)$ the yield of $^{i}Bu_2(^{i}PrO)SiBr$ was lower (85% to total area of the product peaks). The other peaks were ignored.

The isosteric silanes and bromosilanes were prepared as described previously [6]. The products of bromination of substituted triarylsilanes were not isolated, but their identities were confirmed by the addition of H_2O to the reaction vessels after the reactions were complete, which resulted in the rapid dissappearance of the peaks from the triarylbromosilanes.

Preparation of Et_3SiBr

A solution of 0.0032 g (0.006 mmol) of $H_2PtCl_6 \cdot 6H_2O$ in 0.02 ml of $^{i}PrOH$ was added to a stirred solution of 2.1 g (0.018 mol) of Et_3SiH and 4.4 g (0.036 mol) of allyl bromide. The mixture was then heated under reflux for 3 h. After removal of unchanged C_3H_5Br kugelrohr distillation yielded 3.3 g (0.017 mol) of Et_3SiBr. B.p. 65° C (18 torr). The ^{1}H-NMR spectrum was identical with that previously reported [18].

Preparation of Ph_3SiBr

A solution of 0.004 g (0.0077 mmol) of $H_2PtCl_6 \cdot 6H_2O$ in 0.03 ml of $^{i}PrOH$ was added to a stirred solution of 10.3 g (0.039 mol) of Ph_3SiH and 10.1 g (0.083 mol) of allyl bromide. The mixture was then heated under reflux for 2 h. After removal of unchanged C_3H_5Br kugelrohr distillation yielded 13.1 g (0.038 mol) of Ph_3SiBr. B.p. 200° C (1 torr), m.p. 118–120° C. (Lit. m.p. 120–121° C [19]).

GC-equipment: 1 m column of internal diameter 4 mm, 7% SE-30 on Chromosorb W-NAW 80–100 mesh, argon 40 cm^3 min^{-1}, FID-detector. Internal standards used were: C_9H_{20} for $(^{i}PrO)_3SiH$ and $^{i}Bu(^{i}PrO)_2SiH$, $C_{10}H_{22}$ for

$^{i}Bu_2(^{i}PrO)SiH$, $C_{11}H_{24}$ for $^{i}Bu_3SiH$, $C_{17}H_{36}$ for Ph_3SiH, Ph_3SiOMe for (p-$MeC_6H_4)_3SiH$ and squalane for (p-$ClC_6H_4)_3SiH$ and (p-$MeOC_6H_4)_3SiH$.

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