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Electrophilic substitution of organosilicon compounds

I. Model studies of allylation of tert-chlorine ended polyisobutylenes with allyltrimethylsilane

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Summary

Quantitative electrophilic allylation of 2,4,4-trimethyl-2-chloropentane (TMP-Cl) a molecule which closely mimics the tert-chlorine termini of ^{t}Cl-PIB-^{t}Cl by allyltrimethylsilane (AllylSiMe$_3$) has been accomplished and the product 4,4,6,6-tetramethyl-1-heptene (TMP-allyl), a new organic compound, has been characterized by ^{1}H NMR spectroscopy. The synthesis was carried out by the use of Et$_2$AlCl or TiCl$_4$, using CH$_2$Cl$_2$ or CH$_3$Cl or CH$_2$Cl$_2$-C$_6$H$_{14}$ solvent systems in the range from -70 to 0° C. The allylation efficiency sequence of the Lewis acids studied was: Et$_2$AlCl > TiCl$_4$ > SnCl$_4$ >> BCl$_3$. Varying the temperature from -70° to 20°C moderately affected the conversions with lower temperatures being preferable. A dramatic solvent effect was observed: While in the presence of 30% CH$_2$Cl$_2$ both allylation efficiency and rate were very high, in hexanes allylation was strongly retarded. Vinyltrimethylsilane (VinylSiMe$_3$), a potential vinylating agent, was inactive under the same conditions.

Introduction

During the past two decades a variety of organosilicon compounds have been shown to react with various electrophilic reagents (1-5). Reactions may occur with organosilicon compounds containing multiple bonds in α,β, β,γ or γ,δ positions to silicon. Most of these reactions are envisioned to proceed by electrophilic attack leading to an intermediate cation β to silicon (1,2,6). The reaction is highly regioselective due to cation stabilization, mainly by $(p-\sigma)\pi$ conjugation of the empty p orbital by the adjacent σ silicon-carbon bond.

Little work has been done with tert-alkyl halides (7-11). So far only adamantyl(Ad) and tert-butyl (t-Bu) halides have been demonstrated to undergo substitution in the presence of Lewis acids with select unsaturated organosilicon compounds.

No systematic work was carried out to study the reactivities of vinyl and allylsilanes toward electrophiles, particularly tert-alkyl derivatives (1-3). The substitution of 1-Ad-Cl with PhHC=CHSiMe$_3$ in the presence of TiCl$_4$ gave very low yields (~19%)(11). In contrast, substitution was almost quantitative under the same conditions with AllylSiMe$_3$. Some other experimental observations also indicated lower reactivity of vinylsilanes toward electrophiles (12).

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The purposes of these investigations were to study electrophilic substitution of tert-alkyl halides by silanes and, if possible, to develop conditions for the quantitative conversion of tert. halides to vinyl or allyl derivatives. We have been particularly interested in the quantitative allylation of TMP-Cl, a model compound for tert.-chlorine ended PIB's that have recently been synthesized in our laboratories (13). Vinyl or allyl capped PIB's would represent prepolymers that could open avenues toward various new intermediates. This paper concerns allylation of TMP-Cl by AllylSiMe$_3$ under electrophilic conditions, the effect of the nature of the Lewis acid, temperature, concentrations, and the nature of solvent on the yields and culminates in the definition of reaction conditions that lead to quantitative allylation.

Experimental

Materials. Et$_2$AlCl (Ethyl Corp.) was treated with NaCl at 80°C for 2 hr to remove possible EtAlCl$_2$ contaminant and distilled in vacuo. BCl$_3$ (Union Carbide Co.) was condensed from a bottle under N$_2$ in a dry box. TiCl$_4$ (Aldrich Co.) and SnCl$_4$ (Fisher Co.) were used as received. AllylSiMe$_3$ and VinylSiMe$_3$ (Petrarch Inc.) were distilled under N$_2$, purity >98% (by GC).

CH$_2$Cl$_2$ or hexanes were refluxed with fuming sulfuric acid overnight, separated, washed with water, ∿5% aqueous NaHCO$_3$ solution, water, dried over CaCl$_2$, refluxed over CaH$_2$, and distilled over CaH$_2$ into flasks equipped with a Rotaflo stopcock. The CH$_2$Cl$_2$ was distilled in vacuo. N-undecane (Chemical Samples Co.) was stored over 3A molecular sieves. 2,4,4-Trimethyl-2-chloropentane was prepared (14) by hydrochlorination of 2,4,4-trimethyl-1-pentene (Aldrich Co.) and purified by distillation in vacuo; purity >95% (by GC).

Procedures. Reactions of TMP-Cl with unsaturated trimethylsilanes were carried out under N$_2$ in reactors equipped with a Teflon stopcock (when CH$_2$Cl$_2$ or hexanes solvents were used) or in culture tubes in a dry box (when CH$_3$Cl solvent was used). Usually 2 ml of the solvent was transferred with a syringe to a reactor under N$_2$. Then 0.040 ml TMP-Cl, 0.040 ml n-undecane and the proper amount of allyl- or vinyl-trimethylsilane (0- to 4-fold molar excess relative to TMP-Cl) were added with a syringe under N$_2$. When the system reached the desired temperature, the reaction was initiated by adding Lewis acid (0- to 4-fold molar excess relative to TMP-Cl) with a syringe under N$_2$.

The BCl$_3$ gas was liquefied at -70°C and the desired amount transferred under N$_2$ with a pipet to a reactor equipped with a Teflon stopcock. Subsequently the proper amounts of solvent, TMP-Cl, and finally AllylSiMe$_3$ were added to get the same concentrations as used in experiments with the other Lewis acids. The charges were occasionally agitated (all systems were homogeneous) and after 5 to 200 min. poured into saturated aqueous NaHCO$_3$ solution (20 ml); the organic phase was separated and dried over MgSO$_4$. Samples were characterized by ^{1}H NMR spectroscopy and GC analysis.

^{1}H NMR spectra were recorded on a Varian T-60 NMR spectrometer, using CCl$_4$ solvent and SiMe$_4$ internal standard. GC traces were recorded on a Hewlet Packard HP-5750 instrument using a 12 foot column packed with SE-30; He was the carrier gas. Temperature programming was from 25 to 250°C and n-undecane was the internal standard.

Preparation of 4,4,6,6-Tetramethyl-1-heptene (TMP-allyl)
Into a 100 ml round bottom flask equipped with a Teflon stopcock, 35 ml CH_2Cl_2, 1 ml (0.0059 mole) TMP-Cl and 1.2 ml (0.0076 mole) $AllylSiMe_3$ were transferred with syringes under N_2. After the system was cooled to 0°C 0.85 ml (0.0071 mole) Et_2AlCl was added with a syringe under N_2. The charge was occasionally agitated and after 20 min. poured into a saturated aqueous $NaHCO_3$ solution (∿150 ml). The organic phase was separated, dried over $MgSO_4$ and the product was isolated by evaporation of the lower boiling components. The product was ∿95% pure (by GC); isolated (with minor losses during isolation) ∿70%, b.p. 162°C/750 mm Hg, d(20°C) 0.750 g/ml. Figure 1 shows the ^1H NMR spectrum of TMP-allyl together with the assignments.

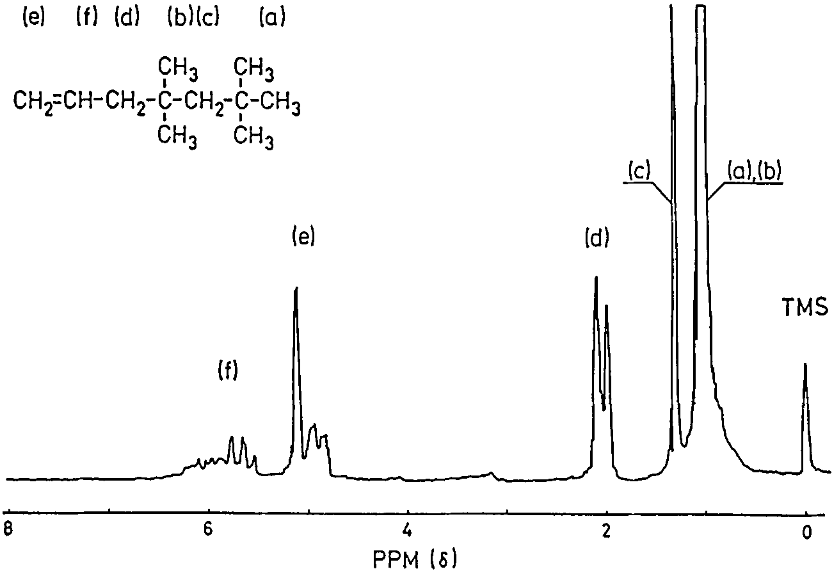


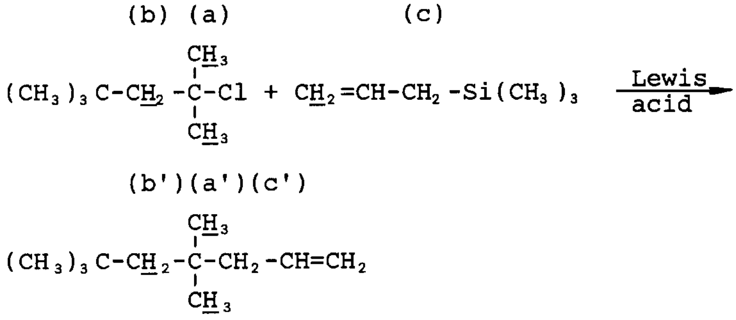
Figure 1. ^1H NMR Spectrum of TMP-allyl

Results and Discussion

First we examined the influence of reaction conditions, i.e., type of Lewis acid, medium polarity, temperature, and time on the yield of TMP-Cl substitution with $AllylSiMe_3$ and $VinylSiMe_3$. Reactions were carried out with $TiCl_4$, or $SnCl_4$, or Et_2AlCl, or BCl_3 in CH_2Cl_2 (3,7). $TiCl_4$ and $SnCl_4$ have been reported to be most active promoters for electrophilic substitution of allylsilanes with tertiary halides (7-11). Et_2AlCl and BCl_3 have not yet been used, however, their examination deemed of interest since these Lewis acids are coinitiators in olefin polymerizations (15).

Experiments with AllylSiMe$_3$

The extent of allylation of TMP-Cl with AllylSiMe$_3$ was followed by ^{1}H NMR spectroscopy, i.e., by determining the changes of the signals of the corresponding CH$_3$- and -CH$_2$-protons adjacent to the quaternary allylated carbon atom. The following resonances have been used:



$$(CH_3)_3C\text{-}C\underline{H}_2\text{-}\overset{C\underline{H}_3}{\underset{C\underline{H}_3}{C}}\text{-}Cl + C\underline{H}_2{=}CH\text{-}CH_2\text{-}Si(CH_3)_3 \xrightarrow[\text{acid}]{\text{Lewis}}$$

$$(CH_3)_3C\text{-}C\underline{H}_2\text{-}\overset{C\underline{H}_3}{\underset{C\underline{H}_3}{C}}\text{-}CH_2\text{-}CH{=}CH_2$$

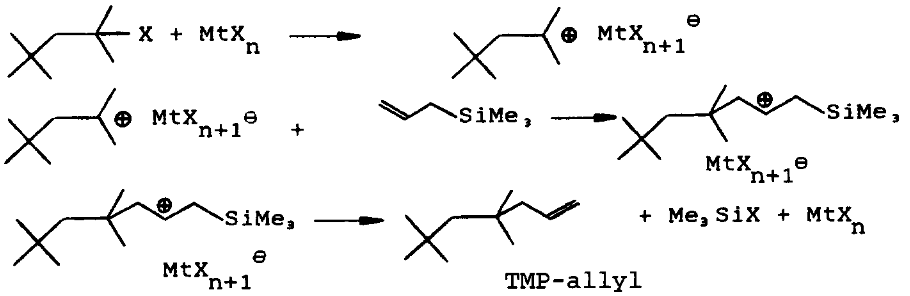
where (resonances in ppm): a = 1.6, b = 1.8, c = 1.45 and 1.6, a' = 1.05, b' = 1.35 and c' = 2.0 and 2.1.

Additional quantitative data have been degenerated by GC analysis. TMP-allyl was synthesized, isolated and its thermal conductivity GC response factor determined. Figure 1 shows the ^{1}H NMR spectrum of this new compound. The formation of TMP-allyl has been followed quantitatively by GC using n-undecane as internal standard.

Table I shows experimental conditions and results. The efficiency of the Lewis acids has been found to decrease as: $Et_2AlCl > TiCl_4 > SnCl_4 >> BCl_3$. Differences in the activities of Lewis acids increased as the temperature was increased. At -70°C allylation was quantitative in the presence of Et$_2$AlCl, or TiCl$_4$, or SnCl$_4$ using a one-fold molar excess of AllylSiMe$_3$ relative to TMP-Cl (Expts. 1,6,11 in Table I).

The above order of the Lewis acid efficiencies does not follow the general sequence of activities of Lewis acids (16); however, it follows the order of coinitiator efficiencies for TiCl$_4$, SnCl$_4$ and BCl$_3$ in isobutylene (16,17) and styrene polymerizations (18) and that found for the acetylation of toluene and racemization of α-phenylethyl chloride (16). Thus the extent of ionization by the Lewis acids governs substitution yield.

The overall mechanism of electrophilic substitution with AllylSiMe$_3$ may be envisioned as follows:



where Mt = Al, B, Sn, Ti; X = Cl, (Cl or Et in Al case). The allylation of TMP-Cl with AllylSiMe$_3$ is very fast in the presence of Et$_2$AlCl, TiCl$_4$ and SnCl$_4$. The reaction is complete in $\sim$10 min. in the -70° to 0°C range and longer times (up to 3 hrs) did not affect the yield (see Tables I, II). Evidently TMP-allyl is quite stable in the reaction mixtures.

TABLE I. Allylation of TMP-Cl by AllylSiMe$_3$ in the Presence of Lewis Acids (TMP-Cl = 0.110 mole/L, CH$_2$Cl$_2$)

Expt	AllylSiMe$_3$ mole/L	Lewis Acid mole/L		Temp. °C	Time min	Yield of TMP-allyl %	
						GC	^{1}H NMR
1	0.220	Et$_2$AlCl	0.130	-70	105	$\sim$100	$\sim$100
2	0.220		0.130	0	45	$\sim$100	$\sim$100
3	0.220		0.130	20	15	91	-
4	0.110		0.110	0	45	90	83
5	0.110		0.110	0	16	95	85
6	0.220	TiCl$_4$	0.130	-70	115	$\sim$100	$\sim$100
7	0.220		0.130	0	45	88	94
8	0.220		0.130	20	15	84	82
9	0.110		0.110	0	103	65	66
10	0.110		0.110	0	16	83	89
11	0.220	SnCl$_4$	0.130	-70	95	95	-
12	0.220		0.130	0	50	86	-
13	0.220		0.130	20	15	52	-
14	0.110		0.110	0	150	37	-
15	0.110		0.110	0	15	40	-
16	0.220	BCl$_3$	0.770	-70	134	3	-
17	0.220		0.770	0	65	15	-
18	0.220		0.690	0	200	13	-
19	0.220		0.420	0	51	30	-
20	0.120		0.143	0	150	2	-

The influence of conditions on TMP-allyl yield may be discussed in terms of competing reactions: 1) Reactions involving carbocations: proton elimination, hydride transfer, olefin addition, i.e., AllylSiMe$_3$ or TMP (as a product of proton elimination from TMP$^{\oplus}$) (19) and 2) Reactions involving AllylSiMe$_3$ and Lewis acids and/or protic impurities: silicon-carbon bond cleavage (1-3, 20, 21) and oligomerization (22). AllylSiMe$_3$ is probably not polymerized by TMP$^{\oplus}$ since the yield of TMP-allyl did not decrease by increasing the AllylSiMe$_3$/TMP-Cl ratio from 1 to 5. Thus AllylSiMe$_3$ may also be useful as a telogen in olefin polymerizations. In the presence of Et$_2$AlCl allylation was essentially quantitative in the -70° to 0°C range. Excess AllylSiMe$_3$ remained unreacted for at least 2 hrs (GC did not show side products).

The efficiency of TiCl$_4$ was close to that of Et$_2$AlCl, or slightly lower above 0°C (compare expts. 3 and 8 in Table I). A small amount of higher boiling side products (b.p. 200° to 300°C by GC) indicated some oligomerization.

The efficiency of $SnCl_4$ is strongly temperature dependent with lower temperatures being preferable (expts. 11, 12, 13 in Table I).

In the presence of BCl_3 low yields (<30%) of TMP-allyl were observed regardless of the temperature (-70° to 0°C), reagent ratio (0- to 6-fold excess relative to TMP-Cl), and time (15 to 200 min) (expts. 16 to 20 in Table I).

The polarity of the medium dramatically affects the allylation of TMP-Cl (Table II). In hexanes allylation was strongly suppressed (12% TMP-allyl), whereas essentially quantitative yields were achieved as the polarity of the medium was increased, e.g., in hexanes: CH_2Cl_2 = 70:30 v/v.

Table II. Influence of Medium Polarity on the Allylation of TMP-Cl with $AllylSiMe_3$ (TMP-Cl = 0.110 mole/L)

No	$AllylSiMe_3$	Lewis Acid mole/L	Temp. °C	Time min	Solvent	Yield % (GC)
1	0.300	Et_2AlCl,0.160	-50	180	CH_3Cl	96
2	0.220	$TiCl_4$,0.130	-70	115	CH_2Cl_2	∿100
3	0.220	$TiCl_4$,0.130	-70	115	$CH_2Cl_2:C_6H_{14}$ = 30:70 v/v	∿100
4	0.220	$TiCl_4$,0.130	-70	155	C_6H_{14}	12
5	0.110	$TiCl_4$,0.120	-55	5	CH_2Cl_2	92
6	0.110	$TiCl_4$,0.130	-55	5	$CH_2Cl_2:C_6H_{14}$ = 30:70 v/v	88

Experiments with $VinylSiMe_3$

The reactivities of $AllylSiMe_3$ and $VinylSiMe_3$ toward TMP-Cl have been compared under the same conditions: [TMP-Cl]= 0.05 to 0.11M, [$AllylSiMe_3$] or [$VinylSiMe_3$] = 0.06 to 0.60M, [$TiCl_4$] = 0.130M or [Et_2AlCl] = 0.08 to 0.32M, CH_2Cl_2 or CH_3Cl, -50° to -35°C. In contrast to complete allylation obtained with $AllylSiMe_3$, vinylation of TMP-Cl did not occur (by GC) even under forcing conditions, i.e., using a 3 to 10 fold molar excess of $VinylSiMe_3$ relative to TMP-Cl for 2-3 hrs. The absence of reactivity of $VinylSiMe_3$ is probably due to steric effects (3). Conceivably, in the case of $VinylSiMe_3$, the developing positive charge cannot be sufficiently stabilized by the Si due to geometric constraints.

Conclusion

On the basis of prior literature references (10,11) and the present data it seems that tert-alkyl halides can be quantitatively allylated with $AllylSiMe_3$ under suitable conditions, i.e., in the presence of Et_2AlCl or $TiCl_4$ in CH_2Cl_2 or CH_3Cl, or CH_2Cl_2-hexanes (>30% CH_2Cl_2) solvents in the temperature range from -70° to 0°C.

Acknowledgement

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