RELATIVE REACTIVITY OF SOME ALKENYLSILANES IN THEIR INTERACTION WITH TRICHLOROSILANE

V.F. Mironov and L.L. Shchukovskaya

N.D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR
Institute of Silicate Chemistry, Academy of Sciences of the USSR

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The addition of hydrosilanes to vinyl- or allylchlorosilanes has been achieved previously either in the presence of peroxides [1, 2] or with a catalyst, namely, platinum on charcoal [3]. The use of these initiators required drastic experimental conditions, making it necessary to resort to reactions in autoclaves. In the present work we used Speier's catalyst (0.1 N solution of $H_2PtCl \cdot 6H_2O$ in isopropyl alcohol [4] for these additions and this made it possible to carry out the reactions under mild conditions at atmospheric pressure in a normal glass apparatus. Moreover, under our conditions the addition proceeded with heat evolution and cooling was required.

In order to determine the relative reactivity of allyl- and vinyltri-chlorosilanes in their reaction with trichlorosilane, we carried out a competing reaction, i.e., one equivalent of trichlorosilane was added to an equimolecular mixture of these alkenyltrichlorosilanes. As a result of this experiment it became clear that vinyltrichlorosilane is more reactive toward trichlorosilane than allyltrichlorosilane as 60.5% of it reacted, while only 40% of $Cl_3SiCH_2CH = CH_2$ reacted.

$$Cl_3SiCH{=}CH_2 + Cl_3SiCH_2CH{=}CH_2 + HSiCl_3 \longrightarrow 0{,}6Cl_3SiCH_2CH_2SiCl_3 +$$
$$+ 0{,}4Cl_3SiCH_2CH_2CH_2SiCl_3 + 0{,}4Cl_3SiCH{=}CH_2 + 0{,}6Cl_3SiCH_2CH{=}CH_2.$$

By a similar competing reaction of $HSiCl_3$ with a mixture of $Cl_3SiCH = CH_2$ and $(C_2H_5)_2CH_3SiCH = CH_2$ it was possible to establish that the second compound is more reactive than the first; 77% of it reacted, while only 23% of $Cl_3SiCH = CH_2$ reacted. Finally, a comparison of the reactivity of $Cl_3SiCH_2CH = CH_2$ and $(CH_3)_3SiCH_2CH = CH_2$ in their reactions with $HSiCl_3$ showed that allyltrichlorosilane (60% reacted) is more active than allyltrimethylsilane (40% reacted)*. Thus, it became clear that the accumulation of negative chlorine radicals at the silicon atom promotes the addition of trichlorosilane to allylsilanes and inhibits its addition to vinylsilanes. The table gives the properties of compounds synthesized for the first time, including α,ω-disilylethanes, obtained by addition of hydrosilanes to various vinylsilanes and subsequent alkylation with RMgX or ArMgX.

EXPERIMENTAL

Vinyldibutylmethylsilane $CH_2 = CH\,(n\text{-}C_4H_9)_2\,SiCH_3$. To $n\text{-}C_4H_9MgBr$, obtained from 48.7 g of magnesium, and 300 g of $n\text{-}C_4H_9Br$ in 0.7 liter of ether, was added 130 g of vinylmethyldichlorosilane [5]. After a day, the flask contents were boiled for 8 hr and then decomposed with 10% HCl. The ether layer and ether extracts from the aqueous layer were dried with $CaCl_2$. After removal of the ether, vacuum distillation of the liquid residue yielded 113 g of vinyldibutylmethylsilane with b.p. 85-86° (15 mm); the yield was 66.5%. The other vinylsilanes given in the table were synthesized analogously.

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* The same conclusion was reached by Topchiev et al., [2], who added hydrosilanes to various allylsilanes in the presence of benzoyl peroxide, and by Petrov et al., [6], who used platinum on charcoal.

Sample No.	Compound	B.p. in °C (p in mm Hg)	n_D^{20}	d_4^{20}	*MR* found	*MR* calculated	Yield in (%)
1	$(C_2H_5)_2CH_3SiCH{=}CH_2$	116,6 (750)	1,4225	0,7504	43,48	43,46	70
2	$(n\text{-}C_3H_7)_2CH_3SiCH{=}CH_2$	158 (742)	1,4330	0,7664	53,02	52,96	55,5
3	$(n\text{-}C_4H_9)_2CH_3SiCH{=}CH_2$	85 (15)	1,4390	0,7810	62,10	62,06	66,5
4	$(C_6H_5)_2CH_3SiCH{=}CH_2$	128,5—129 (1)	1,5716	0,9972	73,99	74,08	51
5	$(\alpha\text{-}C_{10}H_7)_2CH_3SiCH{=}CH_2$	238,5 (3)	m.p. 136,5—137,5°	—	—	—	22
6	$(C_6H_5)_2CH_3SiCH_2CH_2SiCH_3Cl_2$	171—173 (1,5)	1,5561	1,1134	98,02	97,33	85
7	$(C_6H_5)_2CH_3SiCH_2CH_2SiC_6H_5(CH_3)_2$	213,5—214,5 (1)	1,5740	1,0111	117,69	117,89	—
8	$(C_6H_5)_2CH_3SiCH_2CH_2SiCH_3(C_6H_5)_2$	290—292 (3)	m.p. 85—86°	—	—	—	50
9	$(\alpha\text{-}C_{10}H_7)_2CH_3SiCH_2CH_2SiCH_3Cl_2$	259—260 (2)	—	—	—	—	65
10	$(\alpha\text{-}C_{10}H_7)_2CH_3SiCH_2CH_2Si(CH_3)_3$	226 (1)	m.p.	—	—	—	60

Competing reactions. To a mixture of 29 g of vinyltrichlorosilane (0.18 mole) and 3.15 g of allyltrichlorosilane (0.18 mole) with 0.5 ml of Speier's catalyst was added 24.3 g of trichlorosilane (0.18 mole) with stirring. Heat was evolved during the reaction and therefore the rate of $HSiCl_3$ addition was such that the temperature did not rise above 100°. After being boiled for an hour, the contents of the flask were fractionated on a column. We recovered 11.5 g (0.0713 mole) of vinyltrichlorosilane and 19 g (0.108 mole) of allyltrichlorosilane, i.e., 60.5% of $Cl_3SCH=CH_2$ and 40% of $Cl_3SCH_2CH=CH_2$ reacted out of the amounts initially taken.

An analogous reaction with a mixture of 41.5 g of vinyltrichlorosilane (0.257 mole) and 33 g of diethylmethylvinylsilane (0.257 mole) and 35 g of trichlorosilane (0.257 M) with distillation of the product led to the recovery of 32 g of unreacted $Cl_3SCH=CH_2$ (0.198 mole) and 7.5 g of $(C_2H_5)_2CH_3SiCH=CH_2$ (0.0584 mole), i.e., 22.7% of $Cl_3SiCH=CH_2$ and 77% of $(C_2H_5)_2CH_3SiCH=CH_2$ reacted.

An analogous reaction with a mixture of 56.8 g of $Cl_3SiCH_2CH=CH_2$ and 37 g of $(CH_3)_3SiCH_2CH=CH_2$ with 44 of $HSiCl_3$ led to the reaction of 60% of the allyltrichlorosilane and 40% of the allyltrimethylsilane.

1-(Diphenylmethylsilyl)-2-(methyldichlorosilyl)-ethane $(C_6H_5)_2CH_3Si_3CH_2CH_2SiCl_2CH_3$. A small part (~5 ml) of a mixture of 47 g of diphenylmethylvinylsilane and 35 g of methylchlorosilane was placed in a flask and 0.5 ml of Speier's catalyst [4] added to it. A vigorous reaction was begun by gentle heating. The rest of the mixture was added at such a rate that the temperature in the flask did not rise above 100-120°. The flask contents were then heated at 150° for 2 hr. Vacuum distillation yielded 70 g of $(C_6H_5)_2CH_3SiCH_2CH_2SiCH_3Cl_2$ (85% yield).

SUMMARY

1. The relative reactivity of a number of alkenylsilanes in the addition of $HSiCl_3$ to them was estimated.

2. Ten organosilicon compounds that have not been described previously were synthesized.

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* Original Russian pagination. See C.B. translation.