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FREE RADICAL REACTIONS IN SOLUTION

VIII *. RADICAL-INITIATED ADDITION OF TRIALKYLSILANES ACROSS ALKENE C=C BONDS

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Summary

Difficulties in carrying out the free-radical addition of trialkylsilanes (as opposed to trichlorosilane) to alkene C=C bonds are partly due to telomerization competing with the radical transfer step. This can be overcome by the use of a large excess of trialkylsilane, when good yields of adduct are obtained from mono-substituted and 1,2-disubstituted alkenes.

Introduction

The radical-initiated addition of X_3Si–H across alkene C=C bonds was demonstrated in 1947 [2,3]. Good yields were obtained from trichlorosilane, but yields are lower when alkyldichlorosilanes or dialkylchlorosilanes are used, and very poor for trialkylsilanes [3,4]. In view of the poor yields sometimes though not always encountered in these additions [5], and the development of the alternative catalytic method, using chloroplatinic acid or other Group VIII compounds (see e.g. refs 5, 6), interest in the radical-initiated addition of trialkylsilanes across C=C bonds has subsequently been somewhat diminished.

As part of a programme of investigation of the reactions of organosilicon radicals, we were interested in the different behaviour of trialkylsilanes and trichlorosilane, and hoped that an investigation of the difference might lead to the development of conditions for the addition of trialkylsilanes to C=C bonds in improved yield.

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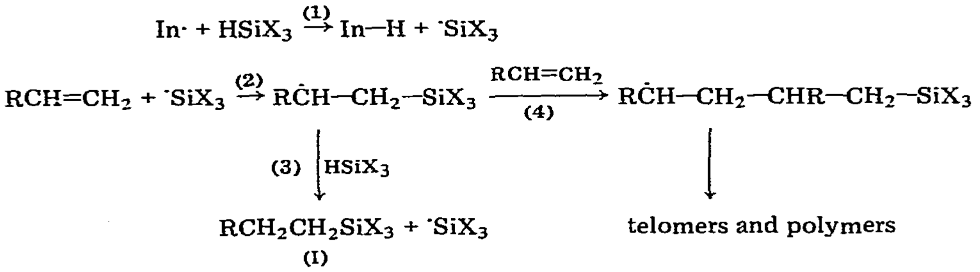
* For part VII see ref. 1.

Results and discussion

We carried out our mechanistic studies on degassed mixtures of organosilicon hydride, alkene, and t-butyl peroxide as initiator in Pyrex ampoules at temperatures of 110—170°C. The radical chain reaction sequence for addition of X_3SiH to alkenes is shown in Scheme 1.

SCHEME 1



$$\mathrm{In}^{\cdot} + \mathrm{HSiX_3} \xrightarrow{(1)} \mathrm{In{-}H} + {}^{\cdot}\mathrm{SiX_3}$$

$$\begin{tikzcd} \mathrm{RCH{=}CH_2} + {}^{\cdot}\mathrm{SiX_3} \arrow[r, "(2)"] & \mathrm{R\dot{C}H{-}CH_2{-}SiX_3} \arrow[r, "\mathrm{RCH{=}CH_2}", "(4)"'] \arrow[d, "(3)"', "\mathrm{HSiX_3}"] & \mathrm{R\dot{C}H{-}CH_2{-}CHR{-}CH_2{-}SiX_3} \arrow[d] \\ & \mathrm{RCH_2CH_2SiX_3} + {}^{\cdot}\mathrm{SiX_3} & \text{telomers and polymers} \\ & \text{(I)} & \end{tikzcd}$$

The low yield of adduct I obtained when trialkylsilanes are used rather than trichlorosilane ($X = Cl$) could be due to a number of reasons. The initiating reaction (1) or either of the two chain propagating reactions (2 or 3) could be significantly slower for ($X = R$) than for ($X = Cl$); alternatively the radical addition process 4 might compete with the transfer reaction (3) and thus reduce the yield.

The idea that reaction 1 is slow in the absolute sense for $X = R$ is ruled out by the ready occurrence of reactions of this type in the photolytic generation of organosilyl radicals in ESR studies [7] at temperatures much lower than those used in the addition reactions. Our product studies indicate that reaction 2 is not a slow step, since substantial quantities of alkene are consumed in the reaction. The presence of substantial quantities of higher boiling products (GLC) in the alkene/trialkylsilane reaction mixtures points to the addition reaction 4 being relatively fast compared with the hydrogen-transfer reaction 3 as the explanation of the low yields when trialkylsilanes are used as the addend rather than trichlorosilane. Our finding that t-alkyl radicals have a selectivity in reaction towards trichlorosilane compared with triethylsilane (by a factor of between 2.3 and 3.1 at 140°C) supports this explanation, and further support is given by our observation that yields can be substantially increased by increasing the [trialkylsilane]/[alkene] ratio to 6/1, thereby diminishing the telomerization reaction 4 in favour of the hydrogen transfer reaction 3 and thus increasing the yield of the desired adduct.

The greater reactivity of $HSiCl_3$ compared with Et_3SiH in reactions of types 1 and 3 may be due to the greater stability of the trichlorosilyl radical [i.e. $D(Cl_3Si{-}H) < D(Et_3Si{-}H)$]. This stability order is supported by reactivity studies of silyl radicals towards CCl_3Br [8], though estimates from kinetic studies of the reactions of X_3SiH with iodine indicate that the trimethylsilyl radical is slightly more stable than the trichlorosilyl radical [9].

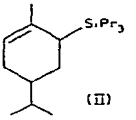
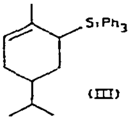
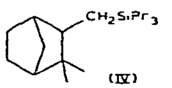
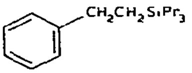
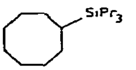
Di-t-butyl peroxide was the best initiator of those tried. Benzoyl peroxide and azoisobutyronitrile gave very poor yields of adduct at 100°C and 80°C, respectively. Relatively high concentrations of t-butyl peroxide were necessary. In experiments at 110°C with $[Et_3SiH]/[1\text{-octene}] = 2$, substantial improvements in product yield took place up to $[(t\text{-}BuO)_2]/[1\text{-octene}] = 0.1$, with rather little effect of further increase in $(t\text{-}BuO)_2$ up to a value of 1.0 in the above ratio. The yield was also insensitive to temperature in the range 110—170°C.

To verify that the reaction is suitable for synthetic use, we carried out a number of reactions on a larger scale and isolated the products. A mixture of the alkene with t-butyl peroxide was added slowly to an excess of the heated organosilicon hydride under nitrogen. This procedure ensured that a very considerable excess of organosilicon hydride over the alkene was present throughout the reaction. The results obtained are shown in Table 1.

Yields are excellent for addition to primary alkenes and good for addition to disubstituted alkenes RCH=CHR', whether open-chain or alicyclic. A moderate yield was obtained from camphene, an alkene of the $RR'C{=}CH_2$ type. The lower yield here may be due to the relative slowness of step 3 for tertiary radicals $RR'\dot{C}{-}CH_2SiR''_3$; we have independent indications from other

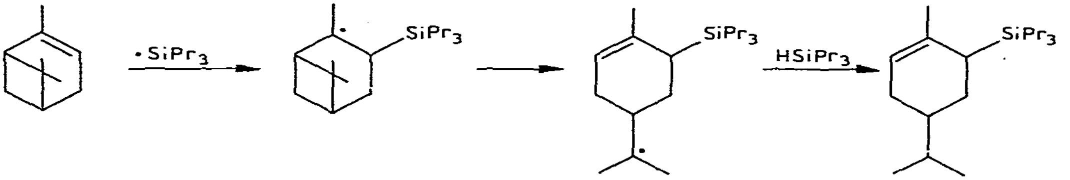
TABLE 1

HYDROSILATION OF ALKENES IN THE PRESENCE OF t-BUTYL PEROXIDE [a]

Silane	Alkene	Product	Yield
Pr_3SiH	1-octene	$n\text{-}C_8H_{17}SiPr_3$	90
Et_3SiH [b]	1-octene	$n\text{-}C_8H_{17}SiPR_3$	91
Pr_3SiH	α(+)-pinene	 (II)	40
Ph_3SiH	α(+)-pinene	 (III)	55
Pr_3SiH	2-octene	$C_8H_{17}SiPr_3$ [c]	60
Pr_3SiH	camphene	 (IV)	45
Pr_3SiH	styrene		1
Pr_3SiH	cyclo-octene		70

[a] Reactions carried out at 140°C by slowly dropping a mixture of alkene (1 mol) and t-butyl peroxide (0.2 mol) on to the heated organosilicon hydride (6 mol) under a nitrogen atmosphere. [b] Reaction mixture refluxed for 24 h after addition complete. [c] Mixture of 2- and 3-octyltripropylsilane.

systems that this is slow [10]. The insignificant yield from styrene is not unexpected; the stabilized benzylic radical $Ph\dot{C}H—CH_2SiPr_3$ formed in the addition step is likely to be very unreactive towards abstraction of hydrogen from tripropylsilane (cf. ref. 11). The ring-opened product obtained when tripropylsilane or triphenylsilane is added to (+)α-pinene (reaction 5) shows that a rearrangement has occurred analogous to that observed earlier in the addition of trichlorosilane to β-pinene [12].



(5)

The procedure described in this paper should therefore provide a useful method for adding organosilicon hydrides to mono-substituted or 1,2-disubstituted alkenes.

Experimental

Ampoule experiments were carried out by introducing the reagents into a Pyrex ampoule, degassing at least three times, and sealing under vacuum. Heating was carried out in a thermostatted oil-bath, and analysis was by GLC. Throughout this paper "mol" indicates relative molar proportions rather than molar quantities.

Table 2 shows selected experiments involving triethylsilane and 1-octene to determine the best reaction conditions. Experiments carried out with benzoyl peroxide (Et_3SiH:1-octene:Bz_2O_2 = 10 : 5 : 1 for 1.5 h at 100°C) and AIBN (Et_3SiH : 1-octene : AIBN = 10 : 5 : 1 for 4 h at 80°C) gave yields of 1-octyltriethylsilane of 5 and 0%, respectively, indicating that these initiators were unsuitable for this reaction.

TABLE 2

ADDITION OF TRIETHYLSILANE TO 1-OCTENE [a]

Et_3SiH	1-octene	$(Bu^tO)_2$	Temp (°C)	time (h)	$n-C_8H_{17}SiEt_3$ (%)
10	10	2	110	96	15
20	10	2	110	96	35
60	10	2	110	96	65
20	10	2	140	4	34
60	10	2	140	4	60
60	10	2	170	0.5	64
20	10	0.5	110	360	10
20	10	1	110	360	35
20	10	2	110	360	36
20	10	5	110	360	41
20	10	10	110	360	37

[a] Experiments carried out in sealed tubes. Quantities in relative molar proportions.

Preparative experiments were carried out at 140°C under nitrogen. A mixture of t-butyl peroxide (0.2 mol) and alkene (1 mol) was added slowly (2—3 drops/min) from a pressure-equalizing Hershberg dropping funnel on to 6 mol of the trialkylsilane while the mixture was stirred magnetically. After addition was complete, the mixture was refluxed for a further 2 h, followed by separation of the desired reaction product, normally by fractional distillation under reduced pressure using a spinning-band column. Physical properties of products (see Table 1) were as follows: Tripropylsilane α(+)-pinene adduct (II), b.p. 150°C/1 mmHg, Raman $\nu = 1655$ cm^{-1} (C=C), M^+ 294, Found: C, 77.4; H, 13.1. $C_{19}H_{38}Si$ calcd.: C, 77.45; H, 13.0%. Triphenylsilane α-(+)-pinene adduct (III), m.p. 219—220°C, Raman $\nu = 1658$ cm^{-1}, Found: C, 84.85; H, 8.2. $C_{28}H_{32}Si$ calcd.: C, 84.8; H, 8.1%. Octyltripropylsilane, b.p. 120°C/2 mmHg, Found: C, 75.5; H, 14.3. $C_{17}H_{38}Si$ calcd.: C, 75.45; H, 14.1%. Tripropylsilane camphene adduct (IV), b.p. 120°C/5 mmHg, M^+ 294, Found: C, 77.7; H, 13.2. $C_{19}H_{38}Si$ calcd.: C, 77.45; H, 13.0%. Cyclooctyltripropylsilane, b.p. 95°C/1 mmHg, M^+ 268 Found: C, 76.1; H, 13.5. $C_{17}H_{36}Si$ calcd.: C, 76.0; H, 13.5%.

Competition of radicals derived from 2-propyl-1-pentene for trichlorosilane and triethylsilane

Mixtures of trichlorosilane (1.0 mol), triethylsilane (1.0 mol), 2-propyl-1-pentene (4.0 mol) and t-butyl peroxide (0.1 mol) were degassed and heated in ampoules at 140°C for 4 h. Final concentrations of Cl_3SiH and Et_3SiH were estimated by NMR, and application of the Ingold-Shaw relationship [13] gave k_{Cl_3SiH}/k_{Et_3SiH} for the reaction

$$R_3SiCH_2—\dot{C}Pr_2 + X_3SiH \rightarrow R_3SiCH_2CHPr_2 + X_3Si\cdot$$

$$(X, R = Et \text{ or } Cl)$$

as 3.1, with no allowance for $HSiCl_3$ consumed by the Bu^tOH produced in the reaction, or 2.3 if it is assumed that each mol of $(Bu^tO)_2$ produces 2 mols of Bu^tOH, which in turn destroy 2 mols of $HSiCl_3$.

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