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NOTE

RATE STUDY OF THE EPOXIDATION OF VINYLTRIALKYLSILANES

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Several epoxyethyl-substituted organosilicon compounds have been prepared by epoxidation of vinylsilanes with peroxy-acid[1-5], but no rate studies of these reactions have been reported. It seemed of interest to compare the reactivities of the vinylsilanes in this reaction, which seems to involve a three-centre transition state[6,★], with those in reactions with carbenes[8-10], which also involve such transition states, and we report the relative rates of epoxidation of vinylsilanes, $R(CH_3)_2SiCH{=}CH_2$ with perbenzoic acid. [During the study, it was found that in the case of vinylpentamethyldisilane both vinyl and disilanyl groups were oxidised, to give (epoxyethyl)-pentamethyldisiloxane[11].]

Four vinylsilanes and 1-heptene were examined, and rates were measured at three temperatures. The second order law was found to be obeyed accurately in all cases. The enthalpy of activation $\Delta H^{\neq}$, and the entropy of activation, $\Delta S^{\neq}$, were calculated by the usual method. The rate constants, $\Delta H^{\neq}$, and $\Delta S^{\neq}$ calculated at 35° are shown in Table 1.

TABLE 1

SECOND ORDER RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE REACTION OF TRIALKYLVINYLSILANES WITH PERBENZOIC ACID IN BENZENE[a]

Compound	$k \times 10^4$ ($l \cdot mole^{-1} \cdot sec^{-1}$)			$\Delta H^{\neq}$ ($kcal \cdot mole^{-1}$)	$\Delta S^{\neq}$ (e.u.)
	25.0°	35.0°	45.0°		
$Me{-}SiMe_2CH{=}CH_2$	2.36	5.15	10.1	13.1	−31.2
$Et{-}SiMe_2CH{=}CH_2$	1.86	4.24	8.49	13.7	−29.6
iso-Pr$-SiMe_2CH{=}CH_2$	1.89	4.45	9.10	14.2	−28.0
tert-Bu$-SiMe_2CH{=}CH_2$	1.77	4.13	7.71	13.3	−31.0
$Me{-}(CH_2)_4{-}CH{=}CH_2$		13.8			

[a] All rate constants are mean values from duplicate or triplicate runs.

The reactivities decreased in the order 1-heptene > $Me_3SiCH{=}CH_2$ > iso-$PrMe_2SiCH{=}CH_2 \simeq EtMe_2SiCH{=}CH_2$ > tert-$BuMe_2SiCH{=}CH_2$, though differences are small for the $RMe_2SiCH{=}CH_2$ compounds. The order for the $RMe_2SiCH{=}CH_2$ compounds can be attributed mainly to an increasing steric effect, since the nucleo-

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[★] However, for an alternative 1,3-dipolar mechanism see ref. 7.

philicity of the C=C bond does not vary significantly for these compounds[12]. The activation parameters did not give further information on the relative importance of the effect; they vary in a compensative manner, as shown in Table 1.

It is of interest to compare the reactivity of a vinylsilane relative to 1-heptene in reactions with various reagents, and pertinent data are listed in Table 2, from which it will be seen that $k(R_3SiCH{=}CH_2)/k$(1-heptene) ratios vary considerably. Attack of free trichloromethyl radicals is least selective. Addition of a free radical can be expected to lead to a less crowded transition state, since it involves terminal attack on the vinyl group, but, as pointed out by Seyferth and Dertouzos[10], both steric and electronic effects must influence the rates, and decrease in nucleophilicity of the C=C bond in vinylsilanes due to $(p\rightarrow d)_\pi$ conjugation may be of importance.

TABLE 2

RELATIVE REACTIVITIES OF C=C DOUBLE BOND TOWARD VARIOUS REAGENTS

Compound	Relative reactivity toward					
	$PhCO_3H$[a] (35°)	$\cdot CCl_3$[b] (80°)	$:CCl_2$[c] (80°)	$:CCl_2$[d] (−30°)	$:CHCO_2Et$[e] (56°)	$:CF_2$[f] (80°)
1-Heptene	1.00	1.00	1.00	1.00	1.00	1.00
$Me_3SiCH{=}CH_2$	0.37	0.95		0.047	0.52	
$EtMe_2SiCH{=}CH_2$	0.31	0.90	0.069			0.26

[a] This work. [b] Addition of $CBrCl_3$[12]. [c] From $PhHgCCl_2Br$[10]. [d] From $CHCl_3$+tert-BuOK reaction[9]. [e] From N_2CHCO_2Et[8]. [f] From Me_3SnCF_3+NaI in DME[10].

It may not be easy to separate effects quantitatively, but the relative electrophilicity of the reagents can be estimated from the reaction constants toward the standard substrates. The Hammett ρ values for substituted styrenes in CCl_3 radical addition[13], CCl_2 (generated from mercurials) addition[14] and epoxidation with perbenzoic acid[15] are -0.43 (with σ^+), -0.619 (with σ^+), and -1.30 (with $\sigma + 0.48\,\Delta\sigma_R^+$), respectively, so that the electrophilicity of these reagents increases in the order $CCl_3^{\cdot} < CCl_2{:} < PhCO_3H$. Thus if only electronic effects operated, epoxidation with perbenzoic acid should give the smallest relative rate ratio, $k(R_3SiCH{=}CH_2)/k$(1-heptene). This is not the case, and it is possible that dichlorocarbenes [produced by the reaction of chloroform with potassium tert-butoxide[9] or from phenyl(bromodichloromethyl)mercury[10]] generate more crowded transition states than the other reagents. In this connection it is noteworthy that CF_2 and $CHCO_2Et$ give "normal" relative rates.

EXPERIMENTAL

Starting materials

All preparations were carried out under dry nitrogen. Trimethylchlorosilane, dimethyldichlorosilane, methyldichlorovinylsilane, and vinyltrichlorosilane were commercial samples.

Vinyltrimethylsilane[16] and vinyldimethylethylsilane[17] were prepared as described in the literature. The boiling points and other physical properties were in excellent agreement with those reported.

Isopropyldimethylchlorosilane. Isopropylmagnesium chloride was prepared and allowed to react with dimethyldichlorosilane concurrently by *in situ* Grignard method[18]. Thus, 50 g (0.637 mole) of isopropyl chloride, 20 g (0.823 g-atom) of magnesium, and 200 g (1.55 mole) of dimethyldichlorosilane were refluxed in 300 ml of tetrahydrofuran for 15 h. After filtration of the salt, excess dimethyldichlorosilane and the solvent were distilled off. Fractionation through a 35-cm column packed with glass helicoils gave 62 g (0.454 mole, 71% yield) of pure (homogeneous to GLC) isopropyldimethylchlorosilane, b.p. 110° (lit.[19]: b.p. 109–110°/738 mm).

When isopropylmagnesium bromide prepared in ether was added to an ethereal solution of dimethyldichlorosilane, no reaction took place. In tetrahydrofuran, however, isopropyldimethylchlorosilane could be obtained but in a low yield. Thus, from 74 g (0.602 mole) of isopropyl bromide, 17 g (0.700 g-atom) of magnesium, and 150 g (1.17 mole) of dimethyldichlorosilane, 25 g (0.182 mole, 30.2% yield) of isopropyldimethylchlorosilane was obtained.

Vinyldimethylisopropylsilane. Vinylmagnesium chloride was prepared from 25 g of magnesium and vinyl chloride in 500 ml of tetrahydrofuran as described previously[20]. Isopropyldimethylchlorosilane (62 g, 0.454 mole) was added and the mixture was refluxed for 10 h. After work-up, fractional distillation gave 22 g (0.17 mole, 37% yield) of pure vinyldimethylisopropylsilane, b.p. 109.5–110°, n_D^{20} 1.4182, d_4^{20} 0.7428, MR_D 43.54 (calcd.: 43.66). (Found: C, 65.40; H, 12.59. $C_7H_{16}Si$ calcd.: C, 65.54; H, 12.57%.) The yield could probably be improved by recovering the material from the forerun.

Vinyldimethyl-tert-butylsilane. This compound was prepared by the same procedure described above from dimethyl-tert-butylfluorosilane and vinylmagnesium chloride in tetrahydrofuran in 70% yield, b.p. 127°, n_D^{20} 1.4281, d_4^{20} 0.7565, MR_D 48.40 (calcd.: 48.31).

Perbenzoic acid. This compound was prepared from benzoyl peroxide by the published procedures[21,22] slight modified by use of dichloromethane as solvent. It was sublimed repeatedly below 30° at a reduced pressure.

Kinetic procedure

A solution of perbenzoic acid in benzene was pipetted into a solution of vinylsilane in benzene contained in a flask immersed in a thermostatted bath. Both solutions were of known concentration and prewarmed to the bath temperature. The zero time of the reaction was taken at the time when half volume of the perbenzoic acid solution had been discharged from the pipette.

Aliquots, usually 2 ml, of the reaction mixture were pipetted into a 2% solution of acetic acid containing an excess amount of potassium iodide. The liberating iodine was titrated with 0.05 N sodium thiosulfate solution by using starch solution as an indicator.

Rate constants were calculated from least squares slopes of plots derived from the second order rate expression.

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