Mechanism of Thermal Eliminations. Part 30.[1] Pyrolysis of 2-Trimethylsilylethanol and 1-Aryl Derivatives

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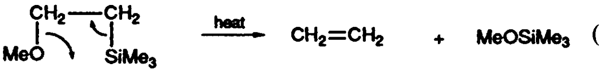
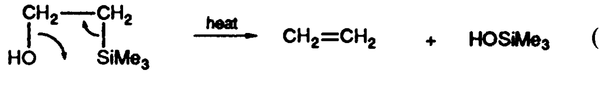
The Arrhenius parameters (E_{act} = 45.57 kcal mol^{-1}, log A/s^{-1} = 12.865) and rate coefficient at 600 K (1.84 × 10^{-4} s^{-1}) for the *cis* β-thermal elimination of trimethylsilanol from 2-trimethylsilylethanol are identical (within experimental error) with those reported in the literature for elimination of methyl trimethylsilyl ether from 1-methoxy-2-(trimethylsilyl)ethane. This indicates that the driving force for the reaction, formation of the Si–O bond, is such that alteration of the nucleophilicity of oxygen has little effect on the reaction rate. A series of 1-aryl-2-trimethylsilylethanols have been prepared and their rates of elimination determined. The activating effect of the 1-aryl substituent (5.2-fold) is much less than the corresponding effect in the pyrolysis of ethyl acetates (63-fold) and 2-trimethylsilylethyl acetates (87-fold). Breaking of the α-C–O bond is thus kinetically less important than in the other reactions, and this conclusion is confirmed by a correlation of the rate data with the Yukawa–Tsuno equation which gives $\rho = -0.4$, $r = 0.3$. Si–O bond formation in the reaction is thereby shown to be of over-riding kinetic importance. For the 4-methylphenyl- and 4-methoxyphenyl compounds a minor competing reaction was the elimination of water to give the corresponding 1-aryl-2-trimethylsilylethene, and this has a higher activation energy than for the elimination of trimethylsilanol. NMR spectra for the 1-aryl-2-trimethylethanols show that interaction between the OH and $SiMe_3$ groups inhibits free rotation about the C(1)–C(2) bond. Preparation of 1-aryl-2-trimethylsilylethanols gave 1,3-diaryl-4-trimethylsilylbutyl trimethylsilyl ethers as byproducts arising from elimination of water from two molecules of the alcohols in a process believed to be two-step.

1-Methoxy-2-(trimethylsilyl)ethane has recently been shown to undergo *cis*-β-elimination to give ethene and methyl trimethylsilyl ether, eqn. (1).[2] This is thus a reaction, further to those which we have described,[1,3] in which nucleophilic attack of oxygen upon silicon provides the driving force for elimination; the strength of the forming Si–O bond is evidently of critical importance. The reaction takes place according to the Arrhenius parameters, E_{act} = 45.1 kcal mol^{-1} and log A/s^{-1} = 12.7. These produce a calculated rate coefficient of 1.86 × 10^{-4} s^{-1} at 600 K.



(1)

In order to learn more about the mechanism of such reactions the thermal stability of the corresponding alcohol, 2-trimethylsilylethanol has been examined. We find that it undergoes a similar reaction, eqn. (2), and we have measured the Arrhenius parameters for the elimination. We have also prepared a series of 1-aryl-2-trimethylsilylethanols and measured the Arrhenius parameters for the corresponding eliminations, eqn. (3).



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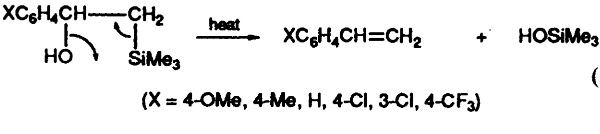

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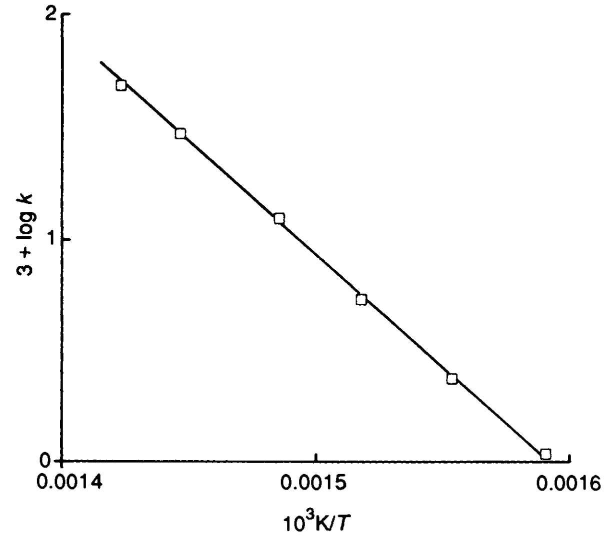


Fig. 1 Arrhenius plot for the pyrolysis of 2-trimethylsilylethanol

Results and Discussion

2-Trimethylsilylethanol.—Thermal decomposition of this compound gave excellent first-order kinetics to beyond 95% reaction, the kinetic data being given in Table 1, and the Arrhenius plot in Fig. 1. The Arrhenius parameters, E_{act} = 45.571 kcal mol^{-1} and log A/s^{-1} = 12.865 are the same, within experimental error, as those given in the literature for pyrolysis of the corresponding ether. Likewise, the rate data predict a rate coefficient at 600 K of 1.84 × 10^{-4} s^{-1}; equal, within experimental error, to the rate coefficient obtained for the ether. The similarity of the reactivities of the two compounds suggests that the difference in nucleophilicities between the OH and OMe groups is unimportant. Evidently the strength of the forming Si–O bond is the dominating feature in determining the overall rates.

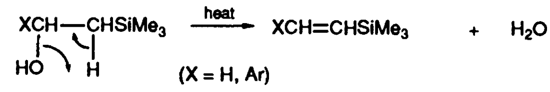
It is relevant at this point to consider why the reaction given

Table 1 Kinetic data for pyrolysis of 1-X-2-trimethylsilylethanols

X	T/K	k/10^{-3} s^{-1}	log(A/s^{-1})	E_{act}/kcal mol^{-1}	Correlation coefficient	k/10^{-3} s^{-1} at 650 K
H	702.6	47.8	12.865	45.571	0.998	4.55
	691.5	29.2				
	673.5	12.4				
	659.0	5.53				
	643.8	2.39				
	628.5	1.06				
4-MeOC$_6$H$_4$	662.7	43.3	12.852	43.020	0.9999	24.7
	647.9	21.8				
	635.2	11.1				
	622.7	5.55				
	612.6	3.23				
4-MeC$_6$H$_4$	662.5	38.0	13.257	44.522	0.9997	19.3
	647.9	16.6				
	635.9	8.94				
	623.3	4.50				
	613.1	2.42				
C$_6$H$_5$	662.6	31.3	13.151	44.466	0.9996	15.8
	647.7	13.75				
	635.2	6.91				
	623.0	3.46				
	612.8	2.03				
4-ClC$_6$H$_4$	662.6	24.1	13.040	44.477	0.9996	12.1
	647.7	10.5				
	635.7	5.37				
	622.6	2.68				
	612.8	1.53				
3-ClC$_6$H$_4$	662.6	19.8	12.790	43.996	0.9990	9.91
	647.9	8.72				
	635.7	4.27				
	623.0	2.30				
	612.9	1.30				
4-F$_3$CC$_6$H$_4$	662.5	17.6	12.845	44.265	0.9996	9.10
	648.1	8.07				
	635.9	4.18				
	623.2	2.19				
	613.1	1.13				

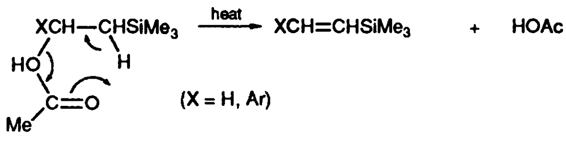
Table 2 Relative rates of pyrolysis of 1-aryl-2-trimethylsilylethanols at 650 K

Substituent	k_{rel}	log k_{rel}
4-OMe	1.54	0.187
4-Me	1.22	0.087
H	1.00	0.0
4-Cl	0.766	−0.116
3-Cl	0.627	−0.203
4-CF$_3$	0.576	−0.240



$$\underset{\mathrm{HO}}{\mathrm{XCH}}-\underset{\mathrm{H}}{\mathrm{CHSiMe_3}} \xrightarrow{\text{heat}} \mathrm{XCH{=}CHSiMe_3} + \mathrm{H_2O} \quad (4)$$

(X = H, Ar)



$$\underset{\substack{\mathrm{HO}\\ \mathrm{Me{-}C{=}O}}}{\mathrm{XCH}}-\underset{\mathrm{H}}{\mathrm{CHSiMe_3}} \xrightarrow{\text{heat}} \mathrm{XCH{=}CHSiMe_3} + \mathrm{HOAc} \quad (5)$$

(X = H, Ar)

by eqn. (2) takes place and not the alternative given by eqn. (4; X = H) (no vinyltrimethylsilane was detected in the products). For pyrolysis of 2-trimethylsilylethyl acetate, eqn. (5; X = H), the β-hydrogen is eliminated in preference to the β-trimethylsilyl group.[3] Elimination of the latter group has a higher activation energy and is only observed at elevated temperatures.[3,4] Thus, Si–O bond formation is less important for elimination from esters and this follows because the transition state for these reactions is more polar than that for elimination of water from alcohols; in consequence there is a greater positive charge on the α-carbon in the transition state. The very strong accelerating effect of a β-SiMe$_3$ group on an adjacent carbocation (carbon–silicon hyperconjugation)[3] is therefore of considerable importance and greatly accelerates the reaction leading to loss of β-hydrogen, so that for esters this reaction is the dominant one.

1-*Aryl-2-trimethylsilylethanols*.—These compounds also gave excellent first-order kinetics, the results of which are given in Table 1. Substituents in the aryl ring gave the activation/deactivation effects expected for a reaction that proceeds *via* formation of a carbocation adjacent to the ring (Table 2). Three features are noteworthy:

(i) First, the rate coefficient for the 1-phenyl compound is only 4.87 times greater at 600 K than that for 2-trimethylsilylethanol. This contrasts with the acceleration by a 1-phenyl group of 63-fold in pyrolysis of ethyl acetate [eqn. (6; Ar = Ph)] and 87-fold in pyrolysis of 2-trimethylsilylethyl acetate [eqn. (5; X = Ph)].[3]

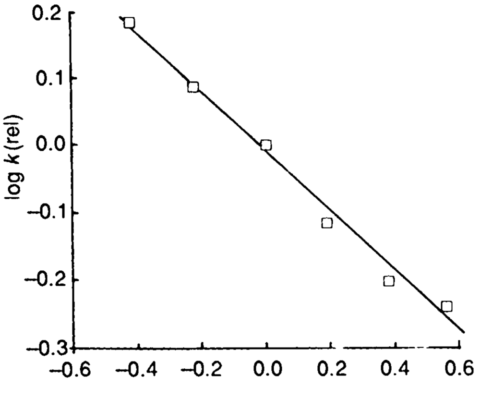
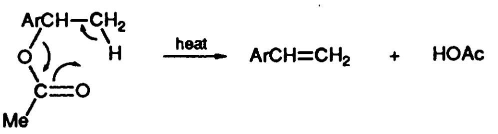


Fig. 2 Hammett correlation for 1-aryl-2-trimethylsilylethanols ($\rho = -0.4$)

This shows that there is very little polar character in the transition state for the reaction. Again this follows from nucleophilic attack of oxygen upon silicon being the main driving force for the reaction.



(6)

(ii) Linear free energy analysis of the reactivity data requires use of the Yukawa–Tsuno equation,[5] with values of $\rho = -0.4$, and $r = 0.3$ (Fig. 2). Both the magnitude of the ρ factor and the low resonance component confirm that there is relatively little charge developed at the side chain α-position in the reaction transition state. Again this contrasts with the larger ρ factors of -0.63 for pyrolysis of 1-arylethyl acetates [eqn. (6)][6] and -0.50 for pyrolysis of 1-aryl-2-trimethylsilylethyl acetates [eqn. (5; X = Ar)],[3] and for both these reactions the r-factors were *ca.* 1.0 so that a direct correlation with σ^+-values was possible. (Note that the ρ factors are not directly comparable to that obtained in the present case because use of the Yukawa–Tsuno equation enhances the ρ factor.)

Overall the results confirm the small amount of charge developed at the side chain α-position in the transition state and this is consistent with nucleophilic attack of oxygen upon silicon being of sufficient importance that other factors play a secondary role.

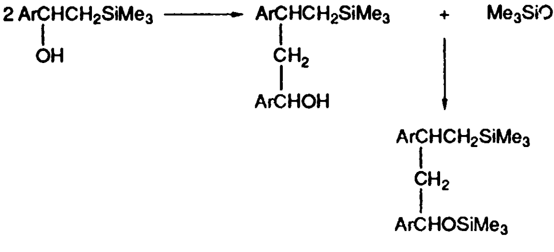
(iii) For the 4-methoxy and 4-methyl derivatives product runs showed that the alternative elimination of water [eqn. (4; X = Ar)] took place to the extent of *ca.* 25% at 705 K and 15% at 660 K. This reaction was not detected with any of the other compounds. Two conclusions follow: first, the elimination of water has the higher activation energy and secondly, it only becomes significant when carbocation formation at the side-chain α-position becomes appreciable so that stabilisation by C–Si hyperconjugation can then occur; side chain carbocation formation will be aided by electron-supplying substituents in the aryl ring.

It is relevant that in preparation of the 1-aryl derivatives (see Experimental) elimination of water was found during work-up of the 4-methyl and 4-methoxy compounds if acid traces were present. Here protonation of the hydroxy group would lead to β-$SiMe_3$-assisted formation of a carbocation at the α-carbon, so promoting the alternative elimination.

The incursion of the side reaction for the 4-methyl and 4-methoxy compounds will result in a contribution to the kinetic data for them at the higher temperatures, though this is not detectable in the Arrhenius parameters. This could account for the quality of the Hammett correlation not being of the standard that is usually obtainable in gas-phase work. The derived ρ factor (insofar as it describes the primary elimination) could be as much as 10% in error, but this does not affect any of the conclusions derived here.

Conformation of 1-*Aryl*-2-*trimethylsilylethanols.*—The NMR spectra of these compounds showed an unusual pattern for the CH_2 protons, consisting of AB quartets (intensity ratios of 1:2:2:1), with each peak being a doublet. The doublets are due to coupling with the adjacent proton, but the other splitting shows that the hydrogens are not equivalent. This is attributed to an attractive interaction between the adjacent silicon and oxygen atoms such that an eclipsed, or near-eclipsed conformation is adopted. One hydrogen is then adjacent to the hydrogen on the C-1 atom, whereas the other is adjacent to the phenyl group. This interpretation is confirmed by the absence of splitting in the spectrum of 2-trimethylsilylethanol.

By-products Obtained During Preparation of 1-*Aryl*-2-*trimethylsilylethanols.*—Some preparations were accompanied by the formation of a secondary higher boiling derivative. These were isolated in the case of the 4-Me and 3-Cl compounds, b.p.s 140 and 174 °C, respectively, at 0.2 mmHg and positively identified from the NMR and mass spectra. The former showed the presence of two aromatic rings (8 H, double multiplets each at *ca.* 7.05, 7.13, 7.19 and 7.32 ppm), CH groups adjacent to CH_2 but in different environments (2 H, multiplet at 4.35 ppm and triplet at 4.0 ppm), CH_2 groups in different environments (4 H, sixteen-peak multiplet consisting of eight doublets between 0.97 and 1.35 ppm), and two $SiMe_3$ groups (9 H singlet at -0.15 and -0.19 ppm). The product from the 4-methyl compound was very similar with additional peaks for Me (3 H, singlets at 2.33 and 2.38 ppm); neither spectrum showed OH singlets. The mass spectra showed peaks at $m/z = 211$ and 213 for the 3-Cl compound and 191 for the 4-Me compound, corresponding to $ArCH(CH_2)CH_2SiMe_2$ (the main peak for trimethylsilyl compounds generally appears at $m/z = M^+ - 15$). Evidently the product (of general formula **1**) is formed by loss of Me_3SiOH from two molecules of the alcohol followed by reaction of Me_3SiOH with the initial byproduct, eqn. (7). Consistent with a mechanism involving loss of OH from the α side chain position to give an incipent carbocation is the fact that no by-product at all was formed during preparation of the 4-trifluoromethyl-substituted alcohol.



$$2\,\underset{\displaystyle OH}{ArCHCH_2SiMe_3} \longrightarrow \underset{\displaystyle \underset{\displaystyle ArCHOH}{CH_2}}{ArCHCH_2SiMe_3} + Me_3SiOH \longrightarrow \underset{\displaystyle \underset{\displaystyle ArCHOSiMe_3}{CH_2}}{ArCHCH_2SiMe_3} \quad (7)$$

1

Experimental

^1H NMR spectra were recorded in $COCl_3$ at 360 MHz on an Bruker instrument with TMS as an internal reference.

2-*Trimethylsilylethanol.*—This was a commercially available sample (Aldrich).

1-*Aryl*-2-*trimethylsilylethanols.*—Each compound was prepared by reaction of the Grignard reagent prepared from trimethylsilylmethyl chloride and the corresponding aryl aldehyde. We observed that for compounds with electron-supplying groups in the aryl ring, all traces of acid had to be avoided in the work-up procedure, otherwise a very rapid elimination of water to give the corresponding substituted styrene occurred. Compounds thus obtained were: 1-(4-*methoxyphenyl*)-2-*trimethylsilylethanol*, b.p. 106 °C/0.2 mmHg; m.p. 35–36 °C; δ_H 7.29 and 6.87 (4 H, d, ArH), 4.81 (1 H, t, CH), 3.81 (3 H, s, MeO), 1.72 (1 H, d, OH), 1.31–1.15 (2 H, m, CH_2) and −0.09 (9 H, s, $SiMe_3$); 1-(4-*methylphenyl*)-2-*trimethylsilylethanol*, b.p. 84 °C/0.45 mmHg; δ_H 7.18–7.11 (4 H, m, ArH), 4.74 (1 H, t, CH), 2.10 (1 H, s, OH), 1.17 (2 H, m, CH_2) and −0.10 (9 H, s, $SiMe_3$); 1-*phenyl*-2-*trimethylsilylethanol*, b.p. 84 °C/1.0 mmHg; m.p. 30 °C; δ_H 7.39–7.18 (5 H, m, ArH), 4.77 (1 H, t, CH), 1.93 (1 H, s, OH), 1.24–1.0 (2 H, m, CH_2) and −0.13 (9 H, s, $SiMe_3$); 1-(4-*chlorophenyl*)-2-*trimethylsilylethanol*, b.p. 98 °C/0.16 mmHg; δ_H 7.31 (4 H, m, ArH), 4.82 (1 H, t, CH), 2.04 (1 H, s, OH), 1.19 (2 H, m, CH_2) and −0.05 (9 H, s, $SiMe_3$); 1-(3-*chlorophenyl*)-2-*trimethylsilylethanol*, b.p. 88 °C/0.16 mmHg; δ_H 7.34–7.17 (4 H, m, ArH), 4.77 (1 H, t, CH), 2.65 (1 H, s, OH), 1.15 (2 H, m, CH_2) and −0.05 (9 H, s, $SiMe_3$); 1-(4-*trifluoromethylphenyl*)-2-*trimethylsilylethanol*, b.p. 70 °C/0.3 mmHg; m.p. 30–31 °C; δ_H 7.61–7.46 (4 H, dd, ArH), 4.90 (1 H, t, CH), 1.98 (1 H, s, OH), 1.20 (2 H, m, CH_2) and −0.03 (9 H, s, $SiMe_3$).

Kinetic Studies.—These were carried out using the stainless steel reactor system according to the method described previously.[7] The stoichiometry of each elimination was 2.0 ± 0.05, and rate coefficients were unaltered by a three-fold variation in the amount of sample taken for each run. Product runs were carried out by passing the alcohols down a column of helices heated to a pre-set temperature, the products being condensed in a cold trap. These products together with any material remaining on the column were removed with deuteriated chloroform, and the extent of the respective eliminations determined by NMR spectroscopy.

Decomposition of each alcohol showed formation of the corresponding styrene with the usual dd, d and d pattern at *ca.* 6.7, 5.7 and 5.3 ppm, respectively, with coupling constants of 11 and 18 Hz. For the 4-methyl- and 4-methoxy-substituted alcohols, two other doublets were observed at 6.35 and 6.80 ppm (4-Me) and 6.225 and 6.75 ppm (4-OMe), J = 19 Hz for each. These are due to the formation of the 1-aryl-2-trimethylsilylethenes through loss of water.

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