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Pyrolytic Elimination of 1-Aryl-2-(trimethylsilyl)ethyl Acetates via Two Distinct Pathways

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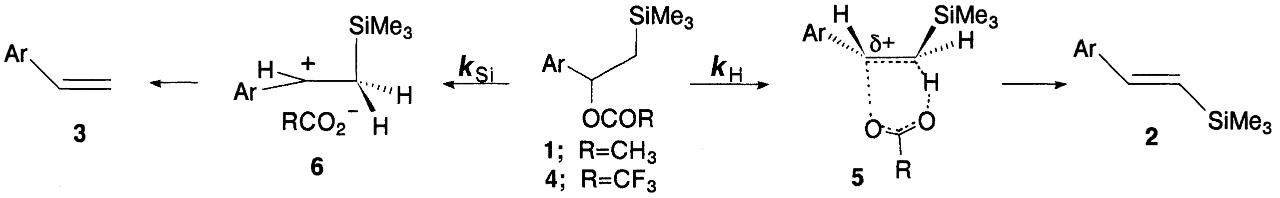
Pyrolysis of 1-aryl-2-(trimethylsilyl)ethyl acetates, X-$C_6H_4CH(OCOR)CH_2SiMe_3$ (X=m-Cl, H, p-Me, and p-MeO; R=CH_3 and CF_3), takes two distinct elimination pathways in varying ratios depending on solvent polarity, electron-supply from aryl groups, and nucleofugality of leaving groups.

Upon heating at 202 °C in xylene, 1-(m-chlorophenyl)-2-(trimethylsilyl)ethyl acetate (**1a**) cleanly gave (E)-1-(m-chlorophenyl)-2-(trimethylsilyl)ethene (**2a**), whereas m-chlorostyrene (**3a**) was obtained when heated in DMSO. Obviously, **1a** undergoes two distinct pyrolysis reactions involving an intramolecular elimination of acetic acid (k_H process) or acetoxytrimethylsilane (k_{Si} process). Table 1 shows the results of pyrolysis of **1a** and related compounds, **1b-1d** and **4a.** The rates of pyrolysis were determined by measuring a time $t_{1/2}$ at which 50% of the ester pyrolyzed. The rate constants for the two pathways, k_H and k_{Si}, could be estimated from the $t_{1/2}$ values and the product ratios **2/3**; the relative rate constants are given in Table 1.



a; Ar=*m*-ClC_6H_4 b; Ar=C_6H_5 c; Ar=*p*-$CH_3C_6H_4$ d; Ar=*p*-$MeOC_6H_4$

Replacement of solvent from xylene to DMSO resulted in a rate acceleration of 2.6×10^3 for the k_{Si} process but a factor of only 2.5 for the k_H process, indicating different responses of the two processes to the solvent polarity. The effect of the leaving group is also striking. The trifluoroacetate **4a** pyrolyzed in xylene very rapidly compared to **1a**, and predominantly gave **3a** in contrast to the exclusive formation of **2a** from **1a**. A good leaving group promotes the k_{Si} process more effectively than the k_H

Table 1. Pyrolysis of **1a**-**1d** and **4a** at 202 °C[a]

Ester	Solvent	$t_{1/2}$[b]	**2**/**3**[b]	Rel. k_H	Rel. k_{Si}
1a	xylene	390 m	0.032	(1.0)	(1.0)
	xylene/DMSO(4:1)	41 m	6.1	1.3	2.5×10^2
	DMSO	4.5 m	33	2.5	2.6×10^3
1b	xylene	59 m	0.054	6.3	10
1c	xylene	17 m[c]	0.084	21	53
1d	xylene	2.7 m[c]	0.23	1.2×10^2	8.6×10^2
4a	xylene	< 1 m[c]	2.03	$>10^2$	$>8\times10^3$

a) Pyrolysis was carried out using 0.1 mol dm^{-3} solutions of esters in the presence of 1.1 equiv. of 2,6-lutidine as an acid quencher.
b) Determined by GLC. c) Determined by NMR.

process. The logarithmic rates of pyrolysis of **1a**-**1d** are correlated with σ^+, yielding ρ^+ values of -1.74 (correlation coefficient R=0.997) and -2.45 (R=0.999) for the k_H and k_{Si} processes, respectively. We previously showed that a solvolytic ionization of **4**, the substituent effect on which exhibits a ρ^+ value of -3.07 (25 °C), leads to the selective formation of **3**.[1)] These findings suggest two different mechanisms, a concerted pathway via the transition state **5**[2)] and an ionic one via the benzylic cation **6** for the k_H and k_{Si} processes, respectively.

It should be noted that the k_H process is accelerated by a β-silyl group. Thus, whereas 1-phenylethyl acetate did not pyrolyze appreciably on heating at 202 °C in xylene for 50 h, **1b** underwent the k_H elimination with a half-life of about 1 h under the same conditions. The ρ^+ value of -1.7 is significantly more negative than a ρ^+ value of -0.66 (600 K) reported for the pyrolysis of 1-arylethyl acetates.[2c)] An E1-like but concerted process is suggested for the k_H elimination for the β-silylated alkyl acetate **1**.

References

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