

THE MECHANISM OF THE THERMAL REARRANGEMENT OF β -KETO-SILANES

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Summary

The rates of thermal rearrangement of a series of 1-(aryldimethylsilyl)-2-propanones have been determined at 150°, 160° and 170°. The reaction is first order in all cases, with energies of activation ranging from 30.6 to 32.9 kcal/mol. A Hammett plot of $\log k$ vs. σ_p gives a ρ value of +0.54, indicating only slight silicon–oxygen bond formation before silicon–carbon bond breaking.

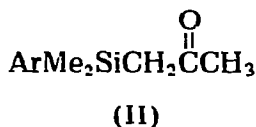
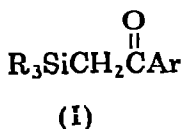
Introduction

Organosilicon compounds with a β -carbonyl group have been shown to have “abnormal” spectral properties and reactivities [2]*.

Brook, MacRae and Limburg [3] have shown that a wide variety of β -ketosilanes undergo a facile, clean, thermal rearrangement to their isomeric silyl enol ethers (eqn. 1). They further showed that the reaction occurs with



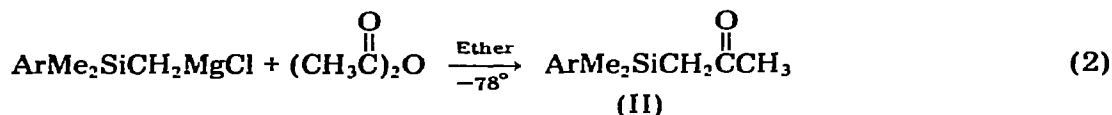
retention of configuration at silicon. More recently, Brook [4] has reported a brief account of the kinetics of the thermal rearrangement of a variety of β -ketosilanes. Of particular interest is the data from a series of *para*-substituted-phenyl β -ketosilanes (I), which showed a ρ value of -0.78 . We wish



* For a review of β -functional organosilanes see ref. 1.

to report here our results of a rate study of the series of 1-(aryldimethylsilyl)-2-propanes (II), which give information about the silicon atom during the reaction.

All of the ketones were prepared from the corresponding chloromethylaryldimethylsilane according to the procedure of Hauser and Hance [5] or of Lutsenko et al. [6] (eqn 2). The kinetic data were taken at 150, 160 and 170°

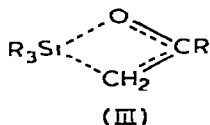


using an IR technique to follow the disappearance of the carbonyl group in the ketone. From this data E_{act} , ΔH^* and ΔS^* were calculated. A Hammett plot of $\log k$ versus σ_p at 160° gives a straight line through all points except that for the *para*-trifluoromethyl derivative. This gives a ρ value of +0.54. Table 1 shows the rate data, the activation parameters and the relative rates for all the compounds studied.

Results and discussion

It can be seen from Table 1 that the activation energies of all compounds studied are fairly constant, falling within a range of 2 kcal/mol. These values are also consistent with those reported by Brook [4]. The entropies of activation are relatively small and negative, which is consistent with the basic four-center transition state proposed by Brook, MacRae and Limburg [3]. The somewhat lower values for ΔS^* for the *p*-chloro and *p*-trifluoromethyl derivatives might reflect a greater ordering of these systems in the ground state, but it is difficult to visualize how this could be at this point.

The above data, coupled with the fact that the reaction is not sensitive to solvent effects [4], lead us to propose a four-centered transition state, III, with very little silicon-oxygen bond formation taking place before Si-C bond breaking occurs.



The fact that the reaction occurs with retention of configuration at silicon [3] rules out a 1,3-sigmatropic rearrangement (if *d* orbitals of silicon are not used) by the Woodward-Hoffmann rules [7]. It is possible that this reaction is just enough of an intramolecular nucleophilic displacement that it can occur with retention of configuration at silicon [8].

Experimental

All solvents were dried by distillation from sodium/benzophenone. The chloromethylaryldimethylsilanes were prepared from chloromethylchlorosilane (PCR) and the appropriate aryl Grignard reagent. The β -ketosilanes were prepared according to the procedure of Hauser and Hance [5]

TABLE 1
KINETIC PARAMETERS FOR THE THERMAL REARRANGEMENT OF β -KETOSILANES IN BENZENE

Aryl group of $\text{ArMe}_2\text{SiCH}_2\text{COCH}_3$	Temp. (°C)	$k \times 10^5$ (sec^{-1}) ^a	E_{act} (kcal/mol)	ΔH^\ddagger (kcal/mol)	ΔS^\ddagger (cal/mol deg)	$k(\text{rel})$ (160°)
Phenyl	150	5.72	30.76 ± 0.4	29.90 ± 0.4	-7.6 ± 0.9	1.00
	160	13.4				
	170	31.5				
<i>p</i> -Tolyl	150	4.63	30.38 ± 0.3	29.50 ± 0.3	-8.9 ± 0.6	0.88
	160	11.8				
	170	25.0				
<i>p</i> -Anisyl	150	4.73	30.90 ± 0.2	30.02 ± 0.1	-7.7 ± 0.3	0.86
	160	11.6				
	170	26.3				
<i>p</i> -Chlorophenyl	150	7.66	32.96 ± 0.1	32.08 ± 0.1	-2.0 ± 0.1	1.38
	160	18.5				
	170	45.2				
<i>p</i> -Fluorophenyl	150	7.45	30.63 ± 0.03	29.76 ± 0.04	-7.5 ± 0.1	1.33
	160	17.8				
	170	38.8				
<i>p</i> -(Trifluoromethyl)- phenyl	150	10.3	31.97 ± 0.1	31.09 ± 0.2	-3.7 ± 0.3	1.88
	160	26.2				
	170	57.4				

^a With the exception of the *p*-tolyl ketone at 150°, which was ± 0.2 all the rate constants showed a deviation of less than $\pm 0.1 \text{ sec}^{-1}$.

or of Lutsenko et al. [6] and were purified by preparative GLC. All new compounds showed satisfactory IR, NMR, and mass spectral data*. Infrared spectra were recorded on a Perkin-Elmer 237 spectrometer, NMR spectra on a Varian T-60 spectrometer and mass spectra on a Hitachi-Perkin-Elmer RMS-4 spectrometer. The kinetic data were treated using an IBM 360 computer. The constant temperature bath was filled with Dow Corning 500 fluid, insulated with vermiculite and agitated with a mechanical stirrer. The temperature control was maintained within $\pm 0.1^\circ$ with a Fisher Proportional Temperature Control.

The general procedure used to follow the rate of the thermal rearrangement of the β -ketosilanes to silyl enol ethers is described below.

A solution of the ketone in benzene was prepared such that the absorbance of the carbonyl band in the IR was about 0.8 (ca. 0.05 M for matched 0.5 mm cells). Concentration studies showed that all the ketones studied obeyed Beer's Law. About 200 μ l of this solution was placed in 33 glass tubes, which had been washed with distilled water and dried. The sealed tubes were tied into groups of three and placed in an oil bath held approximately 5° above the temperature of the constant temperature bath. After about 2 or 3 min the tubes were transferred to the constant temperature bath. When the bath had again come to equilibrium (usually about 3 or 4 min) one group of three tubes was removed and the timer started. All tubes were then removed at various time intervals and quenched in dry-ice/acetone to stop the reaction. A T_m was removed after several hours (i.e. 100% reaction). After all of the samples were collected the carbonyl region of each sample was recorded using matched 0.5 mm cells with benzene as the reference solvent. An average of the three plots of $\log A - A_\infty / A_0 - A_\infty$ vs. time gave the rate constants.

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* A detailed report of the synthesis, physical and spectral properties will be reported later.