

Nucleophilic Cleavage of Substituted Benzyltrimethylsilanes using Tetraalkylammonium Fluoride in DMSO-H₂O Media

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Abstract: The nucleophilic cleavage of substituted benzyltrimethyl-silanes in DMSO-H₂O media using tetraalkylammonium fluoride, TAAF, has been studied. The observed rate constants, pseudo first order rate constants, activation, and thermodynamic parameters have been reported. A mechanism for such cleavage has been proposed. The results fit well Hammett equation. The reaction constant, ρ , value of (6.7) has been reported. The ρ value is consistent with a substantial negative charge developing in the transition state.

Key Words: Benzyltrimethylsilanes, Tetraalkylammonium Fluoride (TAAF), Dimethyl Sulphoxide (DMSO)

Introduction

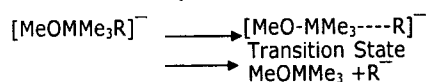
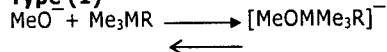
Nucleophilic Cleavage of Benzyl-Silicon Compounds: It is known that cleavage of unsubstituted alkyl and aryl groups from silicon by common nucleophilic reagents is difficult, but using powerful basic reagents such as potassium tert-butoxide in Dimethyl Sulphoxide (DMSO) will cleave even tetraalkylsilanes (Price and Sowa, 1967; Sowa, 1966).

The base cleavage of the Me₃Si-C bond in a compound Me₃Si-R depends on, among other factors, the ability of the R-group to accept the electrons of the Si-R bond, and this ability is related to the stability of the carbanion R⁻, (Eaborn, 1960; Eaborn and Bott, 1965; Eaborn *et al.*, 1975; Alexander *et al.*, 1974; Eaborn *et al.*, 1976) and thus the acidity of the compound RH (Eaborn, 1960; Eaborn and Bott, 1965; Eaborn *et al.*, 1975).

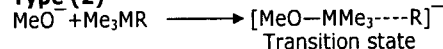


The following mechanisms were suggested by Eaborn and co-workers (Eaborn *et al.*, 1975; Alexander *et al.*, 1974; Eaborn *et al.*, 1976; Maccianttelli *et al.*, 1978), for cleavage of some benzyltrimethylsilanes by methanolic sodium methoxide.

Type (1)



Type (2)



Cleavage of Si-C Bond by Tetraalkylammonium Fluoride

(TAAF): It is known that ionic fluorides behave as peculiar alkaline agents (Knunyants *et al.*, 1947; Nesmeyanov *et al.*, 1948). In view of the high basicity of the fluoride ion in anhydrous aprotic solvents (Rozhkov and Knunyants, 1971) and its high affinity for silicon atom (Pearson, 1963), it might

be expected that ionic fluorides would be active catalysts in nucleophilic substitution reactions.

Alkali metal fluorides require vigorous reaction conditions and long reaction time due to their limited solubility in organic solvents, while TAAF's are soluble in polar organic solvents and their reactions are fast at room temperature or below, but unfortunately, they have their own problems associated with them (Anthous, 1980).

Although the nucleophilicity of TAAF is greatly increased relative to that of metal fluorides, these reagents are also very basic promoting elimination of the substrate-leaving group in addition to displacement. Another problem is that these salts are available only as hydrates or as solutions containing water and it is virtually impossible to dehydrate them entirely. Tetrabutylammonium fluorides (TBAF) and in particular tetraethylammonium fluorides (TEAF), tetrabenzylammonium fluorides are the most active fluorides usually preferred for reactions carried out at or near room temperature, but their low thermal stability precludes their use at temperature above 80°C (Anthous, 1980).

Polar aprotic solvents such as tetrahydrofuran (THF), dimethylformamide (DMF) and dimethyl sulphoxide (DMSO) are usually the best solvents for fluoride-assisted reactions. The apparent driving force for fluoride induced cleavage of C-Si bonds is the formation of the very stable fluorine-silicon bond [$D_{298}^{\circ}(\text{F-Si}) = 541.8\text{kJ/mol}$]. Tetrabutylammonium triphenyldifluorosilicate (TBAT) has been recently used for cleavage of Si-C bonds to initiate C-C bond formation (Pilcher *et al.*, 1995; Pilcher and Deshong, 1996). Tetrabutylammonium triphenyldifluorosilicate is an easily handled crystalline solid that has several advantages over TBAF as a fluoride source; it is anhydrous, nonhygroscopic and soluble in most commonly used organic solvents (THF, toluene, acetonitrile) and solutions of TBAT in these solvents are significantly less basic than the corresponding TBAF solutions.

Materials and Methods

The starting materials used in the preparations of substituted benzyltrimethylsilanes were supplied by Aldrich Chemical Company: Benzyl chloride, p-bromobenzyl bromide, p-methylbenzyl chloride, m-chlorobenzyl bromide, m-trifluoromethylbenzyl bromide, p-chlorobenzyl bromide, p-methoxybenzyl chloride, m-methoxybenzyl chloride, p-tert-butylbenzyl chloride, chlorotrimethylsilane, tetrabutylammonium fluoride hydrate, calcium chloride, sodium sulphate, magnesium turnings, iodine crystals.

The rate measurements at selected wavelengths used to monitor the reactions of substituted benzyltrimethylsilanes were carried out using ATI Unicam-UV/Visible software V-2.11 spectrophotometer. Kinetic measurements were carried out using CPS-240-A-UV/Visible spectrophotometer with thermostatic attachments. The products of cleavage were identified using computerized Fourier Transform Infrared spectrophotometer (Shimadzu FTIR 820 IPC), which has hypride software.

Preparation of Benzyltrimethylsilanes: The following general method was used (Clark *et al.*, 1967). A flame-dried 3-necked round bottomed flask equipped with magnetic stirrer, a double surface-reflux - condenser with calcium chloride drying tube and a pressure equalizing dropping funnel, was charged with magnesium turnings. The reaction was initiated by the addition of few drops of neat alkyl halide and a small crystal of iodine followed by local heating (hair dryer). When the reaction had started the appropriate alkyl halide, diluted with twice its volume of ether (to give an approximately 30% solution) was added at such a rate as to maintain a gentle reflux. After the addition, refluxing was continued for another ½-1 hour and then an ethereal solution of halosilane in ether was added dropwise with stirring. The mixture was heated at reflux for additional 4-8 hours, white slurry of magnesium salts usually formed. The mixture was subsequently cooled and then treated with dilute hydrochloric acid (10%) and extracted with ether. The combined ether extracts were washed with water, dried overnight over anhydrous sodium sulphate. The ether was removed by distillation and the residue was distilled.

General Notes

- 1 An electric vacuum pump was used in distillation at reduced pressure.
- 2 Reaction of m-methoxy-,
- 3 p-methoxybenzyltrimethylsilane with TBAF was not successful eventhough the reaction was repeated twice.
- 4 The number of moles of the protic solvent used in DMSO-protic solvent media was added to DMSO to give a 10-mL solution.

Selection of the Appropriate Wavelengths: The appropriate wavelengths used to monitor reactions between substituted benzyltrimethylsilanes and TBAF were selected as follows:

After addition of a measured concentration of TBAF solution [dissolved in 97-99% (v/v) DMSO/H₂O] to the silane (4-5 mg), the mixture was transferred to a stoppered quartz cell (10 mm path length). The blank solution used in the reference cell was the same as the reaction medium except for the silane. The spectrophotometer was scanned to measure the absorbance in the wavelength range (200-400 nm). The plots of wavelength versus absorbance were monitored at intervals. The wavelength at which the absorbance was shifted toward the substituted toluene region was recorded and used later to monitor that reaction.

The following wavelengths were obtained and used in the rate studies:

C₆H₅ CH₂SiMe₃, 276nm; m-ClC₆H₄CH₂SiMe₃, 280 nm; m-CF₃C₆H₄CH₂SiMe₃, 282 nm; p-ClC₆H₄CH₂SiMe₃, 284 nm; p-BrC₆H₄CH₂SiMe₃, 284 nm; p-CH₃C₆H₄CH₂SiMe₃, 282 nm; p-C(CH₃)₃C₆H₄-CH₂SiMe₃, 280 nm and C₆H₅-CH₂SiEt₃, 278 nm.

Rate Measurements: The technique employed for rate measurements was as follows: 4.2 mg of the benzylsilicon compound was placed in a 5mL volumetric flask and a measured concentration of tetrabutylammonium fluoride (dissolved in 97% DMSO/H₂O) was added to the mark of the flask after preheating to the required temperature. The mixture was shaken and transferred to the quartz uv cell. The absorption readings were recorded at convenient intervals up to about three half-lives; the infinity readings were taken after ten half-lives.

Isolation of the Cleavage Products: A solution of 2.0 g (12.2 mmol) of benzyltrimethylsilane and 4.0 g (12.6 mmol) of TBAF in 20mL aqueous 98% DMSO was refluxed for 8 hours and then added to water. The mixture was extracted by ether followed by washing, drying over anhydrous sodium sulphate, and fractionation of the ethereal layer gave toluene (60%) b.p 111°C, n_D²⁵ = 1.4980. This procedure was applied for all other substituted benzyltrimethylsilanes.

Identification of the Cleavage Products: The identities of the cleavage products were confirmed by:

1. UV/Visible spectrophotometer: A 5 mg of the isolated product was dissolved in 5 mL of aqueous 98% DMSO and transferred to the stoppered quartz cell (10 mm path length). The reference cell was filled with aqueous 98% DMSO. The spectrum obtained was identical with that expected for toluene.
2. Infrared spectrophotometer: The isolated product was diluted with carbon tetrachloride and the spectrum obtained was identical with that obtained for toluene.
3. Thin Layer Chromatography (TLC). TLC was performed for identification of the cleavage product as follows: A silica gel TLC plate was spotted with toluene and the cleavage product using [petroleum ether: ethyl acetate (2:1) as the eluant]. The two compounds gave the same R_f value.

Results and Discussion

In this work, several substituted benzyltrimethylsilanes XC₆H₄CH₂SiMe₃ were prepared as described in the experimental section, (where X: H, p-chloro, p-bromo, p-Me, p-t-Bu and m-trifluoromethyl) and the rates of cleavage of the Si-C bond by tetrabutylammonium fluoride in aqueous 97% DMSO were studied using UV/Visible spectrophotometer.

Determination of the Reaction Order and Rate

Constants: The rates of cleavage of benzylsilanes depend on both the concentrations of silanes and the nucleophile, but since the overall concentration of the nucleophile, (F⁻ and OH⁻) remains constant as indicated from the kinetic results, then the observed rate follows pseudo first order kinetics. The observed rate constants for cleavages of the substituted benzylsilanes were obtained from the slopes of linear plots of ln (A_t - A_∞) versus time. Rates of cleavages of p-Me- and p-CMe₃- benzyltrimethylsilanes at 2.5×10⁻³ M TBAF concentration were very slow. These rates were calculated by comparing the rates of cleavages of p-Me, p-CMe₃ and the unsubstituted silane at TBAF concentration of 0.04 M. Cleavage of benzyltrimethylsilane at TBAF concentration of 0.04 and 2.5×10⁻³M have been determined experimentally.

Substituent Effects in the Cleavage of Benzyltrimethylsilanes: The order of bond breaking or bond forming in most reactions leads to a temporary

development of a positive or negative electrostatic charge at a particular site in the transition-state structure. Determining whether the charge is positive or negative and whether it is relatively large or small allows postulation of the sequence of bond changes. The specific rate constants for cleavage of substituted benzyltrimethylsilane with their substituent constants (σ) are shown in Table (1).

Table 1: Specific Rate Constants for Cleavage of Substituted Benzyltrimethylsilane by TBAF ($2.5 \times 10^{-3} M$) in 97% DMSO at 25°C with their Substituent Constants (σ)

Substituent	σ (Exner, 1972)	$10^{-2} \times k_s$ ($\text{sec}^{-1} \cdot \text{mol}^{-1} \cdot \text{dm}^3$)	$\log k_s / k_{s(0)}$
H	0	0.0288	0.0000
p-Cl	0.24	1.2680	1.6437
p-Br	0.26	2.1400	1.8710
m-Cl	0.37	7.0000	2.3857
m-CF ₃	0.43	13.2400	2.6625
p-t-Bu	-0.15	0.0014*	-1.3133
p-Me	-0.14	0.0017*	-1.2289

*Calculated

A plot of $\log k_s$ against σ gives a straight line with slope 6.7 as shown in Fig. 1. The large value of ρ (viz. 6.7) indicates that the Si-C bond must be broken in the rate determining step, with substantial carbanionic character being developed at the benzylic carbon atom in the transition state. The use of dipolar aprotic solvent in large proportion (97% DMSO) as the reaction media may have an effect on the large value of ρ ; it can not solvate the anions (fluoride, hydroxide and mainly the transition state), so the effect of substituents is more pronounced than those in polar protic solvents.

Effect of Temperature: The rates of cleavage of benzyltrimethylsilane were studied at various temperatures and the specific rate constants are shown in Table 2.

Table 2: Specific Rate Constants for Cleavage of Benzyltrimethylsilane by TBAF ($1 \times 10^{-2} M$) in 97% DMSO /H₂O

T(K)	$10^{-2} \times k_s$ ($\text{sec}^{-1} \cdot \text{mol}^{-1} \cdot \text{dm}^3$)	T(K)	$10^{-2} \times k_s$ ($\text{sec}^{-1} \cdot \text{mol}^{-1} \cdot \text{dm}^3$)
298	3.57	318	17.94
303	7.43	323	29.42
308	9.85	328	40.57
313	13.55	333	54.84

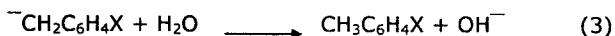
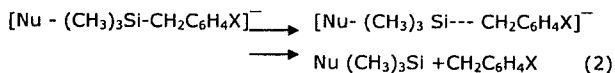
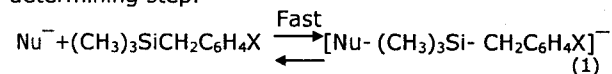
A plot of $\ln K_s$ versus $1/T$ gives a straight line with slope = -7646.90 and intercept 22.77 as shown in Fig. 2. From the slope, E_a was calculated to be 61.26 kJ/mol.

From the slope $\Delta H^\ddagger = 58.22 \text{ kJ mol}^{-1}$, from the intercept $\Delta S^\ddagger = -75.9 \text{ J mol}^{-1} \cdot \text{K}^{-1}$

$$\Delta G^\ddagger = \Delta H^\ddagger - T \Delta S^\ddagger$$

$$\Delta G^\ddagger = 80.8 \text{ kJ mol}^{-1} \text{ at } 298 \text{ K.}$$

Mechanism of Cleavage: The simplest proposed mechanism consistent with experimental observation is the one in which a quinquovalent silicon intermediate is rapidly formed and then decomposes in the rate determining step.



Where Nu^- represents the fluoride and hydroxide anions but mainly fluoride anion. Since the hydroxide anion is produced in step (3) of the reaction.

Hexamethyldisiloxane $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ may be present in the reaction products as a result of a secondary reaction of $(\text{CH}_3)_3\text{SiF}$ with water since $(\text{CH}_3)_3\text{SiF}$ is known to produce $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ in the presence of water and base (Exner, 1972), as shown in the following equations:



Electron withdrawal in X aids the reaction partly by facilitating the approach of the nucleophile to silicon but mainly by increasing the ease of separation of the benzyl group with the electrons of the Si-C bond.

The high reaction constant ρ (6.7) implies a carbanionic character of the benzylic moiety in the transition state of the rate-determining step, so electron-donating substituents (i.e. p-Me, p-t-Bu) destabilize the developing carbanion and slow down the rate of the reaction. The large negative value of ΔS^\ddagger and small value of A indicate that a rigid transition state is formed that supports our proposed mechanism. The question of whether the fluoride ion itself or hydroxide ion from the small amount of water present was the reactive agent for cleavage of benzyl-silicon bond was answered by D.F. Marten and S.M. Wilburn (Martin and Wilburn, 1983) by doing the reaction of silane with hydrated TBAF in the vacuum line. The volatiles were collected in an NMR tube and the major silicon compound was identified as Me_3SiF , but this result does not preclude hydroxide ion as a nucleophile in our work since a relatively large amount of water is present.

Variation of Mole Ratio of Water in H₂O-DMSO Media: The specific rate constants for cleavage of benzyltrimethylsilane by TBAF in various H₂O-DMSO mixtures are shown in Table 3.

Table 3: Specific Rate Constants for Cleavage of $\text{C}_6\text{H}_5\text{CH}_2\text{SiMe}_3$ by TBAF [$0.01 M$] Using Different Mole Ratios of Water in H₂O-DMSO Mixtures at 30°C.

Mole ratio (10^{-2})	$10^{-2} \times k_s$ ($\text{sec}^{-1} \cdot \text{mol}^{-1} \cdot \text{dm}^3$)
3.9	29.9
8.1	10.7
12.2	6.5
16.5	2.7

As shown in Table 3 the rate decreases with the increase of mole ratio of water. As the DMSO content increases the nucleophile becomes less solvated. Since DMSO makes hydrogen bonding with water molecules, so the nucleophile becomes more naked and the reaction media more basic (Jones, 1973). On the contrary, the nucleophile becomes more solvated as the mole ratio of water is increased, since the ability of DMSO to form hydrogen bonding with water molecules decreases as its mole ratio decreases. The mechanism proposed earlier involves dispersal of the negative charge in the transition state. The increasing polarity of the medium as the water content is increased should

lower the reaction rate and this is consistent with our results.

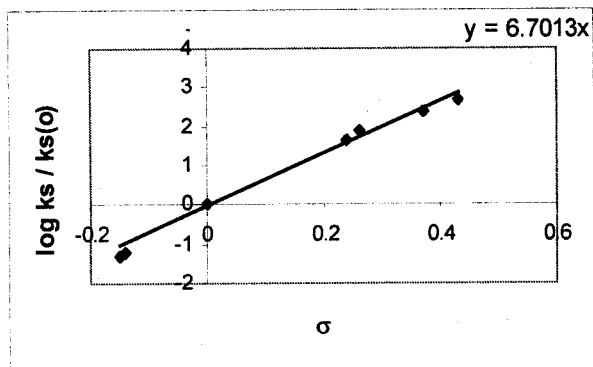


Fig. 1: A Plot of $\log k_s / k_{s(0)}$ Against σ

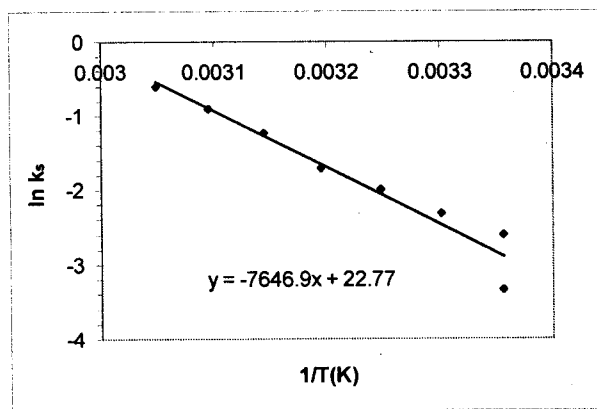


Fig. 2: A Plot of $\ln k_s$ Against $1/T$

Acknowledgement: We wish to thank Dr. Issam R. Abdelraziq of Physics Department for his help in drawing graphs.

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