Journal of Organometallic Chemistry, 73 (1974) 41—48
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CLEAVAGE OF α-HALO-SUBSTITUTED ALKYL GROUPS FROM SILICON

THE EFFECT OF HALOGEN IN THE BASE-CATALYSED SOLVOLYSIS OF (α-DIHALOMETHYL)TRIMETHYLSILANES

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(Received December 20th, 1973)

Summary

The kinetics of the solvolysis of $Me_3SiCHCl_2$ (I), $Me_3SiCHBr_2$ (II), Me_3SiCHI_2 (III) and Me_3SiCCl_2Me (IV) in the system n-propanol/water (8/2 v/v) in the presence of an NH_3/NH_4Cl buffer have been investigated. The results show that α-haloalkyl groups are removed from silicon by two routes: (1) by nucleophilic substitution as a result of attack of a conjugate base of the solvent on silicon, and (2) by base-catalysed ammonia substitution. The existence of the latter route is connected with the fact that α-haloalkyls are very poor leaving groups in nucleophilic substitutions.

The relative reactivities at 25° are as follows, I/II/III/IV = 1/116/246/0.2 for route 1 and I/II/III/IV = 1/24/49/0.05 for route 2.

The reactivity increases with increasing stabilization of the negative charge in the separating carbanion, but there is also evidence that the back-strain in the leaving group affects the reactivity.

Introduction

While investigating cleavage of α-halo-substituted alkyl groups from silicon under conditions of base-catalysed solvolysis we compared quantitatively the reactivities of a series of bromo-, chloro-, and iodo-derivatives. If the process is a nucleophilic displacement at silicon with the haloalkyl group removed from silicon as a carbanion, then since the group has a poor leaving ability, stabilization of the negative charge on the carbanion by the halogen atoms should be important. According to the findings of Hine and co-workers [1] this stabilizing effect increases in the series Cl < Br < I. Against this, facilitation of nucleophilic attack at silicon would be expected to follow the inductive order, Cl > Br > I.

Another aim of our investigation was to gain a deeper insight into the mechanism of the solvolysis of α-haloalkylsilanes in protic solvents in the presence of ammonia buffer, and in particular to throw some light on the participation of the ammonia, as revealed in our earlier studies [2].

The ease of base-catalysed solvolysis of the silicon—α-haloalkyl group bond increases markedly with increase in the number of α-halogen atoms in the leaving group [3]. Monohalogen derivatives react relatively slowly, and there is the possibility of side reactions of the α-halogen substituent. Dihalogen derivatives, on the other hand, readily undergo hydrolysis and alcoholysis in dilute base solutions [4] and serve as convenient substrates for the kinetic investigation of these processes.

We describe below the results of our investigations on the solvolysis of a series of (dihalomethyl)trimethylsilanes, Me_3SiCHX_2, where X = Cl, Br, I, and Me_3SiCCl_2Me. The medium was n-propanol/water (8/2 v/v) catalysed by NH_3/NH_4Cl buffer, and progress of the reaction was followed by measurement of the amount of dihalomethane evolved.

Results

We first confirmed that the reaction gives stoichiometric amounts of the appropriate dihalomethane and that the rate of dihalomethane formation is equal to the rate of substrate decay. The products, in addition to dihalomethane, comprise trimethylsilanol, trimethylpropoxysilane and hexamethyldisiloxane, the last formed by subsequent condensation. The hydrogen atom in the dihalomethyl group of the substrate is incorporated quantitatively in the dihalomethane, as proved by solvolysis of (dichloromethyl)trimethylsilane in system n-PrOD—D_2O*.

We found that for all the substrates the reaction proceeds according to the rate law described in eqn.1.

$$-\frac{d[Me_3SiCHX_2]}{dt} = \left\{k_1 + k_2 \cdot [NH_3]\right\} \cdot \frac{[NH_3]}{[NH_4Cl]} \cdot [Me_3SiCHX_2] \qquad (1)$$

These first-order kinetics are observed for more than 90% of the reactions. Each halogen derivative was studied at various ammonia concentrations and buffer ratios (Table 1). The observed first-order rate constant divided by the buffer ratio was plotted against the ammonia concentration, to give a straight line, from which k_1 and k_2 were determined (Figs.1 and 2). The ionic strength of the medium was kept at a constant level (μ 0.4) by addition of appropriate amounts of lithium chloride. Addition of LiCl, as has already been demonstrated [2], increases the rate in a way typical of a secondary salt effect. The k_1 and k_2 values determined by the least squares method are shown in Table 2 along with the values of thermodynamic functions.

Another series of experiments was performed using a different catalytic system, viz. $N(CH_3)_3/N(CH_3)_3 \cdot HCl$ buffer. In this case the observed rate constant divided by the buffer ratio was independent of the amine concentration (Fig.2), which corresponds to a value $k_2 = 0$ in eqn. 1.

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* The NMR spectrum of the system after reaction reveals the presence of a triplet signal characteristic of $CHDCl_2$ (δ 4.73 ppm), whose area is equal to 1/9 of the signal area of the methyl groups on silicon.

TABLE 1

KINETIC RESULTS OF $Me_3SiCHBr_2$ SOLVOLYSIS
$[Me_3SiCHBr_2]$ 0.23 *M*, μ 0.4, temp. 25°

$[NH_3]$ (*M*)	$[NH_3]/[NH_4Cl]$	$k_{obs} \times 10^5$ (s^{-1})
0.09	11.8	1.46
0.18	11.8	1.54
0.46	11.8	1.89
0.65	11.8	2.63
0.92	11.8	2.81
1.11	11.8	3.46
1.38	11.8	3.79
1.84	11.8	4.46
0.20	54.1	1.51
0.50	21.8	2.06
0.70	15.6	2.50
0.92	11.8	2.80
1.20	9.1	3.36
1.50	7.3	3.84
2.00	5.4	4.96

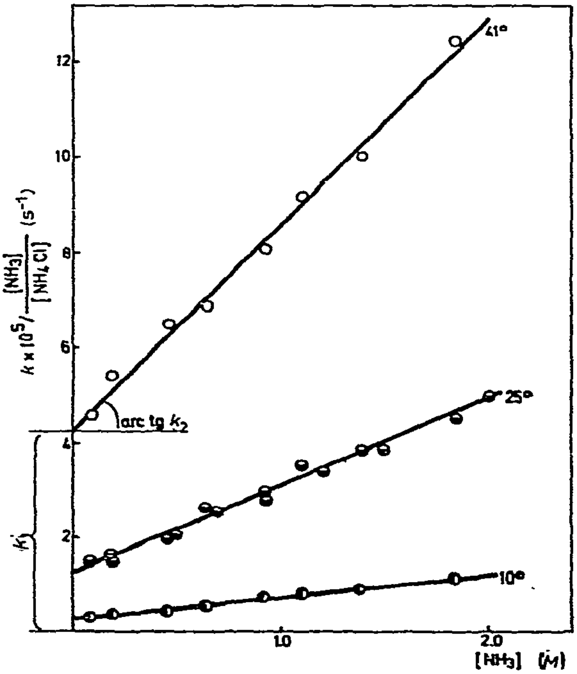

Fig. 1. Dependence of the observed first-order rate constant on the ammonia concentration ($Me_3SiCHBr_2$).

TABLE 2

KINETIC RESULTS[a] OF (α-DIHALOMETHYL)TRIMETHYLSILANES BASE CATALYZED SOLVOLYSIS IN n-PROPANOL/WATER (8/2 v/v) SYSTEM, IONIC STRENGTH μ 0.4

Substrate	Catalyst	Temp. (°C)	$k_1 \times 10^7$ (s^{-1})	$k_2 \times 10^7$ ($l \cdot mol^{-1} \cdot s^{-1}$)	k_2/k_1	$\Delta H_1^\ddagger$ (kcal/mol)	$\Delta H_2^\ddagger$ (kcal/mol)	$\Delta S_1^\ddagger$ ($cal \cdot mol^{-1} \cdot K^{-1}$)	$\Delta S_2^\ddagger$ ($cal \cdot mol^{-1} \cdot K^{-1}$)
$Me_3SiCHCl_2$	NH_3/NH_4Cl	25	0.92 ± 0.5	6.99 ± 0.42	7.59	19.5 ± 1.1			−21.2 ± 3.6
$Me_3SiCHCl_2$	$NMe_3/NMe_3 \cdot HCl$	25	5.94 ± 0.07						
Me_3SiCCl_2Me	NH_3/NH_4Cl	25	0.175 ± 0.031	0.338 ± 0.018	1.93				
$Me_3SiCHBr_2$	NH_3/NH_4Cl	10	24.8 ± 1.4	47.1 ± 1.4	1.90				
$Me_3SiCHBr_2$	NH_3/NH_4Cl	25	107 ± 10	169 ± 10	1.58	15.9 ± 0.3	12.7 ± 0.8	−27.9 ± 1.0	−37.7 ± 2.8
$Me_3SiCHBr_2$	NH_3/NH_4Cl	41	422 ± 22	428 ± 22	1.01				
Me_3SiCHI_2	NH_3/NH_4Cl	10	75.4 ± 11.7	130 ± 12	1.72				
Me_3SiCHI_2	NH_3/NH_4Cl	25	226 ± 19	343 ± 19	1.52	13.0 ± 1.2	11.3 ± 1.0	−36.1 ± 4.1	−41.0 ± 3.2
Me_3SiCHI_2	NH_3/NH_4Cl	41	833 ± 10.5	1030 ± 80	1.24				

[a] The errors are given as standard deviations [12].

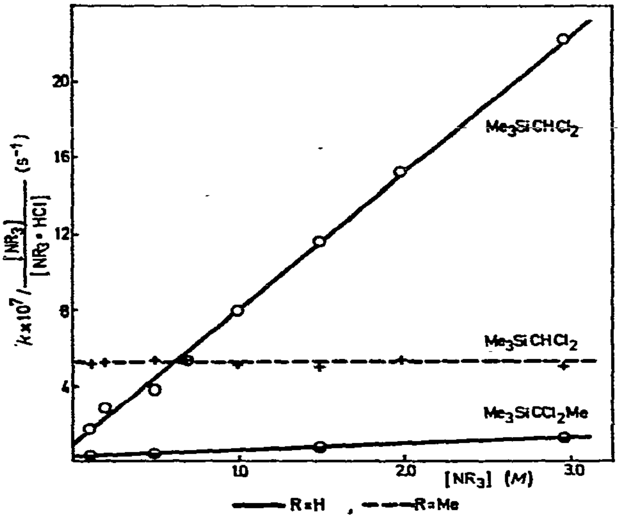

Fig. 2. Dependence of the observed first-order rate constant on the ammonia and the trimethylamine concentration (25°).

Discussion

Mechanism of the solvolytic process

The results confirm the assumption that the solvolyses involve nucleophilic displacement at silicon and electrophilic displacement at carbon [3]. It is clear that neither a carbene nor a substrate conjugate base are involved as intermediates.

The form of the kinetic equation indicates that two parallel processes take place. The rate of the first is directly proportional to the concentration of the substrate and that of the solvent conjugate base OR^- ($R = n\text{-}C_3H_7$ or H) only, which is characteristic of simple base catalysis. The rate of the other component reaction is, however, also dependent on ammonia concentration, which means that the process corresponds to combined catalysis.

The former process may well be assumed to follow the mechanism of direct nucleophilic displacement in which the carbanion CHX_2^- is displaced from silicon by the base OR^-.

$$RO^- + Me_3SiCHX_2 \xrightarrow{\text{slow}} Me_3SiOR + CHX_2^-$$

$$CHX_2^- + ROH \xrightarrow{\text{fast}} CH_2X_2 + RO^-$$

In view of the specific role played by the ammonia molecules the mechanism of the other process is more complicated. The present results seem to support the suggestion made in our previous paper, that the ammonia operates as the nucleophile attacking silicon, so that the rate determining step is OR^--catalysed Si—C bond ammonolysis.

$$NH_3 + Me_3SiCHX_2 \xrightarrow[OR^-]{\text{slow}} Me_3SiNH_2 + CHX_2^-$$

$$CHX_2^- + ROH \xrightarrow{\text{fast}} CH_2X_2 + OR^-$$

$$Me_3SiNH_2 + ROH \xrightarrow{\text{fast}} Me_3SiOR + NH_3$$

The initially-formed trimethylsilylamine is extremely reactive (it has only recently been isolated for the first time [10]) and will be rapidly solvolyzed.

We interpret the role of OR^- in the combined catalysis in terms of general base catalysis. Nucleophilic attack of ammonia on silicon may be synchronous with proton transfer to solvent conjugate base and cleavage of the silicon—carbon bond.

$$RO^{\delta-}\text{----}H\text{----}NH_2\text{----}Si(Me_3)\text{----}CHX_2^{\delta-}$$

The formation of an ammonia—substrate complex in a fast pre-equilibrium reaction is also possible. The kinetically equivalent specific base catalysis involving the formation of NH_2^- in a fast pre-equilibrium reaction seems to be less probable, since the amide ion is unlikely to be present in kinetically significant concentration*. Specific base catalysis could eventually involve fast proton transfer after coordination of ammonia to silicon.

Comparison of reactivities

The changes in reactivity in the series of halogen derivatives studied are similar for both component processes. A distinct rise in the reaction rate is observed on changing from the chloro-, to the bromo-derivative, and a rather small rise from the bromo- to the iodo-derivative. The relative reactivities of the Me_3SiCHX_2 compounds were (X =) Cl/Br/I =1/116/246 for the simple catalysis and 1/24/49 for the combined catalysis. In both cases the increase is due to the distinct decrease in activation enthalpy, since the entropy loss on formation of the activated complex increases markedly from chlorine to iodine. The observed order of reactivity corresponds with that of increased stabilization of the carbanions, as established by Hine in kinetic investigations of base-catalysed isotopic exchange in haloforms [1]. Thus the ability of (α-dihaloalkyl)trialkylsilanes to undergo solvolysis depends primarily on the degree of stabilization of the forming negative charge in the leaving group. The strong effect of the leaving group structure on the reaction rate points to considerable extent of silicon—haloalkyl group bond weakening in the transition state.

The differences in the reactivities of the various halogen derivatives are greater in the case of simple catalysis, indicating that the degree of breaking of the Si—C bonds is greater in this case. In this reaction OR^- is pushing out a carbanion which is a very poor leaving group. The basicity and nucleophilicity of the carbanion HCX_2^- are much higher than those of OR^-. If we assume that in the transition state both the anions have an equal chance of leaving, then in the activated complex the Si—O bond must be nearly formed while the Si—C bond must be almost broken. In the case of combined catalysis the nucleophilic species resembles NH_2^-, which is a considerably stronger base than OH^- or OPr^- [pK_a $(NH_3) = 35$; pK_a $(H_2O) = 15.75$], so the extent of Si—C bond breaking in the

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* Using the crudely estimated value 10^{-35} mol/l for $[NH_2^-]\cdot[H_2O^+]/[NH_3]$ in water [11] an NH_2^- concentration greater than 10^{-25} mol/l is unlikely.

transition state does not need to be so great. Accordingly the energy barrier is lower and the stabilization of negative charge by halogen is less important, as shown by our results. The fact that the combined catalysis by $NH_3 + OR^-$ can compete here with the much simpler route involving substitution by OR^- reflects the importance of the nucleophilicity of the reagent which attacks silicon in the nucleophilic cleavage of Si—C bonds.

It is noteworthy that the steric effect of the leaving group is also important and operates in favour of simple catalysis. Such a conclusion may be drawn from a comparison of reactivities in the cleavage of α-dichloromethyl and α-dichloroethyl groups. As could be expected in view of the destabilizing effect of the methyl group on the carbanion, the α-dichloroethyl is less readily removed than the α-dichloromethyl group in both types of catalysis. The contribution of the combined catalysis in the α-dichloroethyl derivative solvolysis is, however, unexpectedly smaller. This can be accounted for in terms of the steric effects of the leaving group, which makes more difficult the formation of a more crowded transition state in the base—nucleophile catalysed reaction, since the back-strain in the α-haloalkyl compound is released to a lesser extent in the activated complex in this process.

Experimental

General remarks

GLC analyses were performed with a Willy Giede GCHF 18/3 or a Jeol Model 1100 gas chromatograph equipped with flame ionization detectors, with 2 m columns containing 15% LAC-1R-296 on 60/80 mesh Chromosorb P-AW-DMCS. The carrier gas was nitrogen at a flow-rate of 40 ml/min. Column temperatures were 105° for $Me_3SiCHBr_2$ and Me_3SiCHI_2, and 70° for Me_3SiCCl_2Me. NMR spectra were recorded with a Tesla BS-487C spectrometer.

Materials

The (α-dihaloalkyl)trimethylsilanes, all known compounds, were prepared by published methods [2,6—8]. Solid Me_3SiCCl_2Me was purified by recrystallization, and liquids by fractionation through an efficient column. GLC analysis revealed no impurities in the samples used. Deuteropropanol (n-PrOD) was prepared by Quinan's method [9].

Rate studies

The method previously employed [2] was used. In the case of $Me_3SiCHBr_2$, Me_3SiCHI_2 and Me_3SiCCl_2Me, cumene, n-pentadecane and benzene were employed as internal standards for the quantitative GLC determination of the dihaloalkane evolved.

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