Journal of Organometallic Chemistry
Elsevier Publishing Company Amsterdam
Printed in The Netherlands

THE CLEAVAGE OF ETHYNYLSILANES BY ALCOHOLIC SOLUTIONS OF ALKALI HALIDES

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(Received May 23rd, 1966; in revised form August 16th, 1966)

INTRODUCTION

A kinetic study of the facile cleavage of several substituted (phenylethynyl)-silanes and -germanes by aqueous-methanolic sodium hydroxide has been reported by Eaborn and Walton[1]. By comparison (alkylethynyl)silanes appear to be somewhat more stable to dilute alkalies[2]. Both (alkyl- and arylethynyl)silanes are said to be considerably more stable to acid[2,4], whereas the compounds $[(HC{\equiv}C)_3Si]_2O$ and $(C_6H_5C{\equiv}C)_2Si(OC_2H_5)_2$ are reported to hydrolyze readily in water[5]. The only apparent reported instance where a metal salt assisted the cleavage of a silylacetylene involved a mixture of mercuric sulfate and sulfuric acid in methanol[6]. We wish to report here our results on the ready cleavage of silylacetylenes by solutions of certain alkali halides in alcohols.

EXPERIMENTAL

Reagents

The ethynylsilanes were prepared by the reaction of trimethylchlorosilane with the appropriate ethynyl Grignard reagent. Boiling points agreed well with various literature values; the purity of each compound was checked by vapor phase chromatography. Alkali halides were used as obtained from various commercial sources as were methanol, absolute ethanol, n-butanol and tert-butanol.

Although the cleavage of silylacetylenes by HX compounds is very slow, the cleavage in the presence of very small amounts of base is very rapid. For example, glassware washed in alcoholic-KOH and not rinsed with acid was found to release sufficient hydroxide ion into solution to cause spurious and unreliable results.

Trace water, if present, was easily detected by the formation of small quantities of hexamethyldisiloxane during the course of a reaction, and at no time produced an adverse effect on the course or rate of reaction.

Technique

All reactions were carried out under nitrogen. Aliquots were withdrawn periodically with a hypodermic syringe through a serum cap and analyzed directly by vapor phase chromatography with a silicone SF-96 on 60/80 firebrick column. Each analysis was programmed from 65 to 250° at 8°/min. and the detector and injector ovens were at 250 and 300°, respectively. Identification was made by comparison of the relative retention times with those of pure reactants and products under the same instrument conditions. Physical separation of several reaction mixtures verified the assignments in those cases. The formation of acetylene gas was determined volumetrically for the reactions involving trimethylsilylacetylene and bis(trimethylsilyl)acetylene.

DISCUSSION

The results of some of our studies on the relative effectiveness of alkali metal halides in causing cleavage of silylacetylenes $R{-}C{\equiv}C{-}Si(CH_3)_3$ according to reaction (1) are shown in Tables 1 and 2. Thus alkali halides appear to catalyse this reaction

$$R{-}C{\equiv}C{-}Si(CH_3)_3 + R'OH \xrightarrow{MX} R{-}C{\equiv}C{-}H + R'OSi(CH_3)_3 \qquad (1)$$

inasmuch as the rate of reaction is dependent upon the concentration of X^- and each of the acetylenes studied was found to be unaffected by refluxing ethanol after several days in the absence of alkali halides. Eaborn and Walton[1] have shown that the rate of cleavage of $YC_6H_5C{\equiv}C{-}$ from silicon by alcoholic base is a normal function of the electronic character of Y and decreases with an increase of the negative charge buildup on silicon in the transition step. Our qualitative observations indicate a similar effect with respect to cleavage in the presence of KF in that the order $R = C_6H_5 > H = Si(CH_3)_3 > n\text{-}C_4H_9 > tert\text{-}C_4H_9$ is found.

TABLE 1

CLEAVAGE OF $R{-}C{\equiv}C{-}Si(CH_3)_3$ BY SATURATED SOLUTIONS OF VARIOUS ALKALI HALIDES IN REFLUXING ABSOLUTE ETHANOL

R	*Molar conc. of silylacetylene*[a]	*Alkali halide*	*Degree of cleavage*
C_6H_5	0.58	KF	100% (0.3 h)
H[b]	0.79	KF	100% (0.75 h)
$Si(CH_3)_3$	0.52	KF	100% (1 h)
$n\text{-}C_4H_9$	0.55	KF	60% (3 h)
$tert\text{-}C_4H_9$	0.65	KF	60% (6 h)
C_6H_5	0.58	NaF	50% (3 h)
$n\text{-}C_4H_9$	0.55	NaF	13% (20 h)
C_6H_5	0.58	KI	50% (10 h)
C_6H_5	0.58	KCl	0% (72 h)
C_6H_5	0.58	KBr	0% (72 h)
C_6H_5	0.58	NaCl	0% (48 h)
C_6H_5	0.58	NaBr	0% (72 h)
C_6H_5	0.58	NaI	0% (72 h)

[a] Molar conc. at room temperature. [b] Reaction temperature 50°.

At least two mechanistic pathways may be written which would yield the overall result expressed in equation (1). The first sequence, reactions 2–4, involves initially a nucleophilic displacement of an ethynyl anion by halide ion. This is followed

$$(CH_3)_3Si{-}C{\equiv}C{-}R + X^- \rightarrow (CH_3)_3SiX + R{-}C{\equiv}C^- \qquad (2)$$

$$R{-}C{\equiv}C^- + R'OH \rightarrow R{-}C{\equiv}C{-}H + R'O^- \qquad (3)$$

$$R'O^- + (CH_3)_3SiX \rightarrow (CH_3)_3SiOR' + X^- \qquad (4)$$

by two rapid reactions involving proton transfer and displacement of halide from silicon by alkoxide.

TABLE 2

CLEAVAGE OF $C_6H_5{-}C{\equiv}C{-}Si(CH_3)_3$ BY HOMOGENEOUS SOLUTIONS OF ALKALI METAL HALIDES IN METHANOL AND ETHANOL AT 44°

Molar conc. of MX	*Molar conc. of $C_6H_5{-}C{\equiv}C{-}Si(CH_3)_3$*	*Solvent*	*Degree of cleavage*
KF 0.018	0.47	CH_3OH	50% (190 min)
NaF 0.018	0.47	CH_3OH	50% (650 min)
KI 0.018	0.47	CH_3OH	0% (1200 min)
KF 0.018	0.47	C_2H_5OH	50% (150 min)
NaF ~0.004 (sat. soln.)	0.47	C_2H_5OH	5% (1200 min)
KI 0.018	0.47	C_2H_5OH	0% (1200 min)

An alternate reaction mechanism is shown in reactions (5)–(7). The initial step in this reaction is merely a rapid equilibrium solvolysis of the alkali halide.

$$R'OH + MX_{(solv)} \rightleftarrows R'O^-_{(solv)} + M^+_{(solv)} + HX_{(solv)} \qquad (5)$$

$$(CH_3)_3Si{-}C{\equiv}C{-}R + R'O^-_{(solv)} \rightarrow (CH_3)_3Si{-}OR' + R{-}C{\equiv}C^- \qquad (6)$$

$$R{-}C{\equiv}C^- + R'OH \rightarrow RC{\equiv}CH + R'O^-_{(solv)} \qquad (7)$$

Alkoxide ion, or something resembling alkoxide ion, generated according to reaction (5) then effects a nucleophilic displacement of the ethynyl anion from silicon. Protonation of the ethynyl anion should be rapid especially since there is considerable hydrogen bonding of solvent to the acetylenic π system.

Although the data suggest a nucleophilic mechanism, the observations with potassium salts that fluoride is more reactive than iodide and that bromide and chloride are ineffective in causing cleavage are incongruous with the usually observed order of nucleophilic attack at tetrahedral carbon: $I^- > Br^- > Cl^- > F^-$. This order, which is opposite to the order predicted from the base strengths of the ions, is thought to reflect the strength of interaction with solvents, and especially protic solvents[7,8]. Recognizing the relative basicities of these ions, our results are readily interpreted in the following manner. Iodide ion, which should be considerably less encumbered by solvent molecules than either chloride or bromide, may possibly form a pentacoordinate intermediate with the silylacetylene which in the same or a subsequent step is rapidly converted to a trimethylalkoxysilane. Failure to observe formation of trimethyliodosilane under these conditions would be a result of this rapid solvolysis. We suggest that the cleavage of the ethynyl–silicon bond by iodide ion is most reasonably represented by the first mechanistic sequence.

In contrast, the expected strong association of fluoride ion with solvent might hinder primary nucleophilic attack by fluoride at silicon. Furthermore, the absence of a trend in the relative effectiveness of different halides ions in assisting cleavage suggests that fluoride ion and iodide ion influence the reaction course in different manners. We suggest that the second mechanistic path in reactions (5)–(7) is more reasonable for the reactions involving fluoride than is the first reaction sequence. The equilibrium process as shown in reaction (5) represents the extreme conditions for solution of a metal halide in an alcohol. Although one may argue in terms of ion pairs, solvated ion pairs, etc., the fact remains that the alcohol protons will be held, or hydrogen bonded, most tightly to the strongest base in the halide series, namely fluoride ion. The stronger the hydrogen bond to the halide ion, the greater will be the detachment of the alcohol proton from oxygen, and the more the residue will resemble an alkoxide ion. This alkoxide may therefore be considered to be the actual nucleophile. Support for this argument is provided by the observation that triethylfluorosilane (0.70 *M*) in ethanol which has been saturated with potassium fluoride is cleaved to the extent of about 40% after heating at reflux for 24 hours. This solvolysis in the presence of potassium fluoride is unexpected since a solution saturated in fluoride ion would be expected to strongly suppress formation of the alkoxysilane. Of course, the formation of potassium bifluoride may also be an important factor in the position of equilibrium of this reaction. In contrast, triethylfluorosilane, which is cleaved stoichiometrically by sodium ethoxide in ethanol within the time of mixing at room temperature, is solvolyzed by refluxing ethanol to the extent of less than 2%. Most important, potassium iodide must not be extensively solvolyzed according to reaction (5) since the equilibrium between triethylfluorosilane and triethylethoxysilane is not affected after 24 hours at reflux in ethanol saturated with potassium iodide. We therefore favor the second mechanism for the mode of solvolysis of ethynylsilanes by alcohols containing potassium or sodium fluoride even though the arguments are necessarily circumstantial. Allen and Modena[9] used a similar argument to rationalize small salt effects caused by chloride ion on the rates of alcoholysis of chlorosilanes. Their work has been discussed by Eaborn[10]. The failure of chloride and bromide ion to induce cleavage in the present study may then indicate that the nucleophilic character of these ions under these conditions is insufficient to induce cleavage directly by attack at silicon or indirectly via association with the solvent. Alternatively, ion pairing, such as may be the case with sodium iodide, may be too great to provide sufficient charge separation necessary to allow for an efficient nucleophilic attack.

The greater rate of cleavage by potassium salts compared to sodium salts is easily rationalized since ion association between potassium and "alkoxide" ions would be expected to be less than between the somewhat smaller sodium ion and "alkoxide" ion. Furthermore, at 80° the rates of reaction are no doubt more rapid than at 44° primarily because more extensive dissociation of all ion pairs, to form solvent separated ion pairs, is expected at the higher temperature. The small difference for potassium fluoride in the two solvents ethanol and methanol might indicate that potassium fluoride is dissociated to a larger extent in alcohols than is sodium fluoride for which a larger dependence on solvent is noted. The relative rates with sodium fluoride are somewhat greater in methanol ($\varepsilon = 33$) than in ethanol ($\varepsilon = 24$) as expected on the basis of the greater ionizing ability of the former solvent. Solvents of somewhat lower dielectric constant such as the various propyl and butyl alcohols are less useful in this reaction. In addition to the lower ionizing power of these solvents, the maximum concentrations obtainable for solutions of the alkali halides are considerably less than in methanol and ethanol. Identical arguments may be used to explain the greater catalytic effect of potassium iodide over sodium iodide.

In order to test the efficacy of fluoride ion in assisting solvolytic displacement of other groups from silicon, the compounds trimethylphenylsilane, trimethylvinylsilane, trimethylbenzylsilane and trimethylallylsilane were heated at reflux in ethanol saturated with potassium fluoride. The phenyl and vinyl groups did not appear to be cleaved under these conditions. After six days, trimethylallylsilane had been cleaved to the extent of 35% and trimethylbenzylsilane was only minimally cleaved (1–2%) under the same conditions. This is not surprising in that an acetylide ion is a more highly stabilized species than either an allyl or benzyl anion and as such should behave as a better leaving group in what is probably an S_N2–Si reaction.

ACKNOWLEDGEMENT

Financial support and funds for purchase of gas chromatographic equipment were provided by the National Science Foundation (GP-2826).

SUMMARY

Solutions of certain alkali halides in alcohols have been found to readily cleave the ethynyl C–Si bond with formation of alkoxysilane and an acetylene. The relative rates of cleavage are a function of the anion ($F^- > I^-$) and the cation ($K^+ > Na^+$). Chloride and bromide ions were found to be ineffective in causing cleavage. The results are interpreted in terms of the nature of species present in alcohol solutions of alkali halides. Trimethylallylsilane and trimethylbenzylsilane are less readily cleaved than ethynylsilanes under these conditions. Cleavage of phenyl or vinyl groups from silicon was not observed.

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