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Silicon-carbon bond cleavage of pentacoordinate anionic silicates by *N*-bromosuccinimide[†]

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Summary – Silicon-carbon bonds in diaryltrifluorosilicates $[ArPhSiF_3]^-,K^+\bullet$18-crown-6 are readily cleaved by *N*-bromosuccinimide (NBS) in THF to give the corresponding aryl bromides. The reactivity of silicon-aryl bonds towards the NBS cleavage decreases in the following order : 4-$MeOC_6H_4$ > 4-MeC_6H_4 > C_6H_5 > 4-ClC_6H_4 > 4-$CF_3C_6H_4$, with $\rho = -3.0$ in the Hammett plots. The reactivity of 2,6-xylyl group is 10 times greater than that of phenyl group in the intramolecular competition, indicative of no steric hindrance effect. The NBS cleavage of pentacoordinate silicates seems to proceed through the direct electrophilic attack by the positive bromine atom on the Si-ipso carbon not via any hexacoordinate species in the rate-determining step.

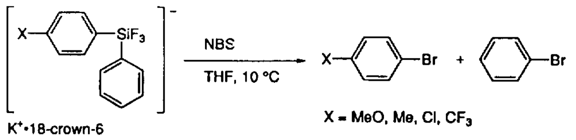
silicon-carbon bond / pentacoordinate silicates / *N*-bromosuccinimide

Introduction

The silicon-carbon bonds in ordinary tetracoordinate organosilicon compounds are generally inert to *N*-bromosuccinimide (NBS) [1a]. We have previously found that silicon-carbon bonds in hexacoordinate silicon compounds such as $[RSiF_5]^{2-},2K^+$ [1a,b] and neutral diorganophthalocyaninatosilicon $[(Pc)SiR^1R^2]$ [1c] (where Pc = phthalocyaninato) are cleaved by NBS under mild conditions. Recently, we have also reported the cleavage of silicon-carbon bonds in pentacoordinate anionic silicates, $[RR'SiF_3]^-,K^+\bullet$18-crown-6 by hydrogen peroxide and proposed the plausible mechanism which involves hexacoordinate silicon species in the transition state [2]. In this paper, we describe the first example of silicon-carbon bond cleavage in pentacoordinate silicates by NBS. The reaction mechanism is compared with that of the oxidative cleavage by H_2O_2.

Results and discussion

Diaryltrifluorosilicates [3] $[ArPhSiF_3]^-,K^+\bullet$18-crown-6, react readily with NBS in THF even at 10°C (scheme 1). Table I summarizes some representative results of the relative reactivities in the intramolecular competition between Si-Ph and Si-Ar bonds in the fluorosilicates. A typical reaction procedure is as follows. A mixture of diaryltrifluorosilicate, NBS (0.5 equiv) and dry THF was stirred at 10°C in the dark. The reaction was monitored by GLC. After 60 min, conversion was higher than 80% based on NBS and no side reaction was observed by the ^1H NMR measurement. The product ratios were essentially constant during the reaction period of 10-120 min, indicative of the greatly reduced reactivity of the silicon-carbon bond in the resulting monoaryl-silicon species.



Scheme 1

Entries 1-4 show the reactivity order of the parent and *para*-substituted phenyl groups. The electron-donating substituents accelerate the cleavage of the aryl-silicon bond (entries 1 and 2), while electron-withdrawing groups greatly slow down the cleavage (entries 3 and 4). The reactivity of *para*-substituted phenyl-silicon bonds decreases in the order : MeO > Me > H > Cl > CF_3. This reactivity order in the intramolecular competition reaction is similar to that of the NBS cleavage in neutral hexacoordinate $[(Pc)SiR^1R^2]$ [1c].

Entry 5 shows the representative result of intramolecular competition of an *ortho*-substituted aryl silicate. The 2,6-xylyl-Si bond is much more reactive than the phenyl-Si bond because of the electronic effects of two electron-donating methyl groups; the 2,6-xylyl group

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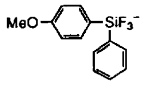
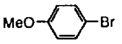
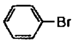
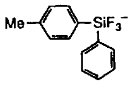
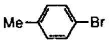
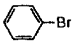
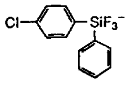
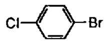
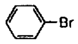
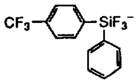
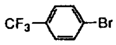
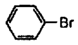
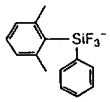
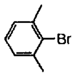
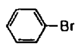
[†] Dedicated to Professor Raymond Calas in recognition of his outstanding contribution in the field of organosilicon chemistry.

[*] Correspondence and reprints

Table I. Relative reactivity of two aryl groups in $[ArPhSiF_3]^-,K^+\bullet$18-crown-6 toward the NBS cleavage[a].

Entry	Silicate	Products ratio[b]		total yield[b]
1		 >10	 : 1	91
2		 6.3	 : 1	76
3		 0.43	 : 1	38
4		 0.035	 : 1	47
5		 13 16	 : 1 (+10 °C) : 1 (−25 °C)	38 34[c]

[a] Carried out with 0.5 equiv of NBS in THF at 10°C in the dark. [b] Total yield based on NBS and product ratio were determined by GLC after 60 min. [c] Overnight.

exhibits little steric hindrance effect in the NBS cleavage reaction [4]. This is in sharp contrast to the steric hindrance observed in the H_2O_2 oxidation [2]. Thus, the electronic effect of substituents becomes a dominant factor in the NBS cleavage.

Hammett plots of the intramolecular relative reactivities of the parent phenyl (product yield : Y_0) vs substituted phenyl groups (product yield : Y) in the pentacoordinate diarylsilicates $[ArPhSiF_3]^-$ are compared between the NBS cleavage and the H_2O_2 cleavage [2], as visualized in figure 1. The ρ value of the NBS cleavage is negative ($\rho = -3.0$), as opposed to that of the oxidative cleavage by H_2O_2 ($\rho = +0.35$) [2b], and the absolute value is much larger in the former. Thus, it is apparent that the NBS cleavage of the silicates is mechanistically different from the oxidative cleavage which may involve the hydrogen peroxide attacking on the silicon atom to form a hexacoordinate species in the transition state. A plausible mechanism on the basis of these experimental results is shown in scheme 2. The NBS cleavage of diarylsilicates is thus considered to proceed by the electrophilic mechanism involving the direct attack of a positive bromine on the Si-ipso carbon center, whose electron density is linearly correlated with the electronic effect of *para*-substituents [3b].

The present study has provided novel results concerning the direct electrophilic cleavage of the silicon-carbon bonds activated by anionic pentacoordination [5]. In this connection, it should be noted that hypercoordinate silicon cation species have recently been prepared by electrophilic cleavage of the silicon-hydrogen bond(s) in neutral hypercoordinate silicon hydrides [6].

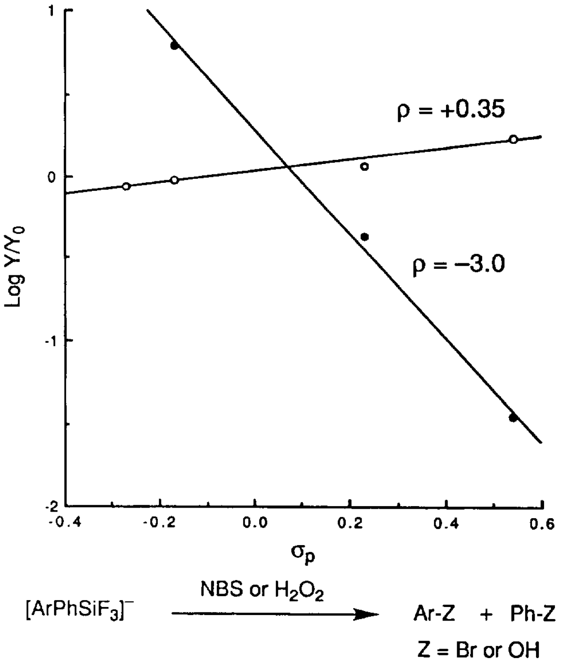
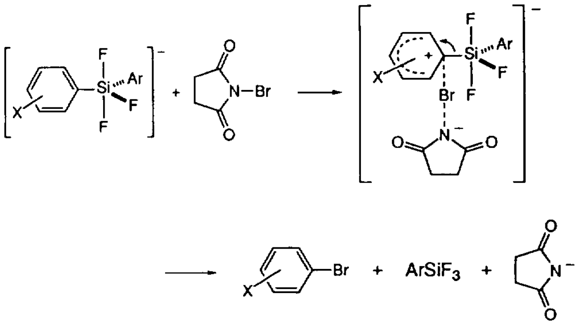


Fig 1. Hammett plots for NBS cleavage (•) and H_2O_2 cleavage (o) (ref 2) of relative reactivities between the parent phenyl (Y_0) and the substituted phenyl group (Y) in pentacoordinate diarylsilicates by intramolecular competitions under the conditions : NBS (0.5 equiv) or 90% H_2O_2 (0.5 equiv) in THF at 10°C.



Scheme 2

Experimental section

General remarks

Gas-liquid chromatography was conducted on a Shimadzu GC-8A gas chromatography equipped with a 1 m column packed with 30% Silicon DC550 on Celite 545. GC peak integrals were recorded with a Shimadzu Chromatopack C-R3A. The reaction temperature was controlled by a NESLAB CC-60II Cryocool equipped with NESLAB Cryotrol.

Materials

Tetrahydrofuran (THF) was distilled under nitrogen from sodium/benzophenone ketyl and stored with molecular sieves (4 Å). *N*-Bromosuccinimide was obtained from

Wako Pure Chemical Industries Ltd. Diaryltrifluorosilicates as their K^+•18-crown-6 salts, $[(4\text{-}CH_3OC_6H_4)PhSiF_3]^-$, $[(4\text{-}CH_3C_6H_4)PhSiF_3]^-$, $[(4\text{-}ClC_6H_4)PhSiF_3]^-$, $[(4\text{-}CF_3C_6H_4)PhSiF_3]^-$, and $[(2,6\text{-xylyl})PhSiF_3]^-$ were prepared according to the slight modification of Damrauer's method [3].

Reaction of silicates with N-bromosuccinimide

A 25 mL test tube equipped with a magnetic stirring bar and a serum cap was charged with a silicate (6.25×10^{-5} mol), undecane as an internal standard for GLC analysis, and THF (2.5 mL). The solution temperature was maintained at +10°C (±0.5°C), while 200 μL (0.5 equiv, 3.125×10^{-5} mol) of a THF solution of NBS (1.56×10^{-1} M) was added by a pipette in one go. A 200 μL aliquot of the solution was withdrawn every 30 min and subjected to GLC analysis (glass column, 1 m, Silicon DC550, 70-180°C, nitrogen gas). Bromobenzene and substituted bromobenzenes were identified by comparison of the GLC retention times with those of the authentic samples. The product yields were determined quantitatively by GLC by using the internal standard.

Acknowledgment

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