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ATTEMPTED GENERATION OF HALOCARBENES: PROTODESILYLATION OF DIHALOMETHYLSILANES

GERALD L. LARSON * and CARLOS CÁDIZ *
Department of Chemistry, University of Puerto Rico, Rio Piedras, P.R. 00931 (U.S.A.)

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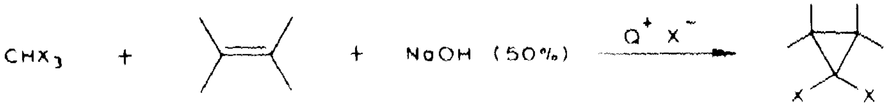
Summary

Attempts to generate chlorocarbene or bromocarbene from (dichloromethyl)-trimethylsilane and (dibromomethyl)trimethylsilane, respectively, under phase transfer conditions results in protodesilylation. The protodesilylation of 1,1-dihalosilanes under phase transfer conditions appears to be general. Phase transfer conditions are also useful for the protodesilylation of other organosilanes.

Introduction

The discovery of the phase transfer entries into dihalocarbenes has been a most remarkable advance in the utility of these species even when one considers the rather harsh alkaline conditions necessary for the reaction [1] (eq. 1). Although this reaction has met with much success for the generation of dihalocarbenes, it has not proved useful for the generation of monohalocarbenes such as chlorocarbene or bromocarbene. In fact dichloromethane is a useful cosolvent for the reaction shown in eq. 1.



(1)

(X = Cl, Br)

Two pieces of evidence in the literature indicate that a dihalomethylsilane, wherein the silicon may be considered equivalent to an "active hydrogen", might generate halocarbenes (eq. 2). Cunico and Chou [2] have shown that

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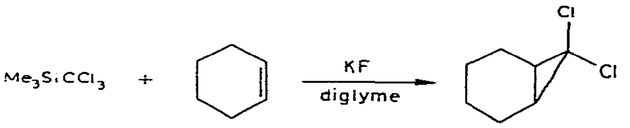
* Graduate student on NIH-MBS grant (RR-08102-09).

$$\mathrm{Me_3SiCHX_2} + \mathrm{NaOH}\ (50\%) \xrightarrow{\text{catalyst}} \mathrm{Me_3SiOSiMe_3} + \underset{\displaystyle :\mathrm{CHX}}{\underset{\downarrow}{\bar{\mathrm{C}}\mathrm{HX_2}}} \qquad (2)$$

(trichloromethyl)trimethylsilane reacts with potassium fluoride in diglyme in the presence of an olefin to give the dichlorocarbene adduct (eq. 3). We have observed that (dichloromethyl)trimethylsilane reacts with aqueous sodium hydroxide under phase transfer conditions to give hexamethyldisiloxane and dichloromethane (eq. 4) [3].



(3)

$$\mathrm{Me_3SiCHCl_2} + \mathrm{NaOH}\ (50\%) \xrightarrow{\mathrm{Q^+\ X^-}} \mathrm{Me_3SiOSiMe_3} + \mathrm{CH_2Cl_2} \qquad (4)$$

Results

Since our initial results indicated that an oxygen nucleophile was sufficiently active to attack the silicon of a 1,1-dihalomethylsilane, it was decided to attempt the generation of chloro- and bromo-carbene employing conditions similar to those used by Makoza and others [1,4]. The results are shown in Table 1 (entries 1 and 2). All of these reactions lead to protodesilylation and no carbene formation. Even the use of a large excess of the olefin and organic cosolvents did not shift the reaction to carbene formation, but gave only protodesilylation.

We then turned our attention to phase transfer conditions that should not favor rapid protonation of the dihalomethyl anion. Therefore, (dichloromethyl)- or (dibromomethyl)-trimethylsilane was treated with alkali metal alkoxides in an aprotic solvent with crown ether catalysis and an excess of olefin (eq. 5). These reactions also lead to protodesilylation with no carbene derived products being observed. Various combinations of the silane ($\mathrm{Me_3SiCHCl_2}$; $\mathrm{Me_3SiCHBr_2}$, $\mathrm{PhMe_2SiCHCl_2}$ and $\mathrm{Et_3SiCHCl_2}$) base (KOH (s), LiOMe, KOMe, KO-t-Bu) solvent (neat olefin, hexane, toluene, THF), and catalyst ($\mathrm{BzEt_3N^+\ Cl^-}$, 18-crown-6,12-crown-4) all gave protodesilylation. In all of these reactions the base was pulverized and dried in a vacuum oven several hours prior to use.

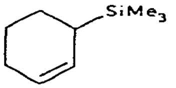
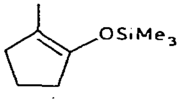
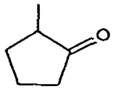
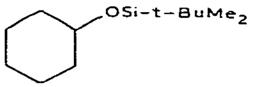
$$\mathrm{Me_3SiCHX_2} + \mathrm{MOR} \xrightarrow[\text{or } \mathrm{Q^+\ X^-}]{\text{crown ether}} \mathrm{Me_3SiOR} + \mathrm{CH_2X_2} \qquad (5)$$

Since protodesilylation is the obvious preferred reaction pathway when dihalomethylsilanes are treated with oxygen nucleophiles under phase transfer conditions it was decided to investigate the generality of this reaction. Indeed, 1,1-dihaloalkylsilanes can be protodesilylated with aqueous sodium hydroxide under phase transfer conditions to give the corresponding 1,1-dihaloalkanes in good yield (eq. 6). The results of this study are shown in Table 1 (entries 1—9). Some observations should be noted. These are: (1) the 1,1-dihaloalkylsilane

$$\mathrm{Me_3SiCX_2CH_2R} \xrightarrow[\mathrm{Bu_4N^+HSO_4^-}]{\mathrm{NaOH}\ (50\%)} \mathrm{Me_3SiOSiMe_3} + \mathrm{HX_2CCH_2R} \qquad (6)$$

TABLE 1

PROTODESILYLATIONS ACCORDING TO EQ. 6

Entry	Organosilanes	Conditions [f]	Product	Yield (%) [a]
1	$Me_3SiCBr_2{}^nC_4H_9$	rt/3 h	$n\text{-}C_4H_9CHBr_2$	47
2	$Me_3SiCBr_2{}^nC_5H_{11}$	rt/3 h	$n\text{-}C_5H_{11}CHBr_2$	49
3	$Me_3SiCCl_2{}^nC_4H_9$	rt/3 h	$n\text{-}C_4H_9CHCl_2$	50
4	$PhMe_2SiCCl_2{}^nC_4H_9$	reflux/12 h	$n\text{-}C_4H_9CHCl_2$	57
5	$Me_3SiCCl_2CH_2Ph$	rt/3 h	$PhCH{=}CHCl$	82
6	$Me_3SiCCl_2CH_2CH{=}CH_2$	rt/3 h	[b]	
7	$PhMe_2SiCCl_2CH_2Ph$	reflux/12 h	$PhCH{=}CHCl$	57
8	Me_3SiCCl_2H [c]	rt/3 h	$n\text{-}C_4H_9CHCl_2$	55
9	Me_3SiCCl_2H [d]	rt/3 h	[b]	
10	$Me_3SiCHCl{}^nC_4H_9$	rt/3 h	[e]	
11	$Me_3SiCHClCH_2Ph$	rt/3 h	$PhCH{=}CH_2$	99
12	Me_3SiCH_2Ph	rt/3 h	$PhCH_3$	79
13	$Me_3SiC{\equiv}CPh$	rt/3 h	$PhC{\equiv}CH$	66
14		rt/3 h	[e]	
15		rt/3 h		98
16		rt/3 h	[e]	

[a] Isolated yield. [b] A mixture of products was formed. [c] Anion formed with LDA in THF and alkylated with n-butyl bromide and the crude reaction product protodesilylated. [d] Anion quenched with allyl chloride and crude reaction product protodesilylated. [e] Only starting material recovered. [f] rt = room temperature.

need not be purified prior to protodesilylation for the reaction to succeed (entry 8); (2) When R is phenyl the ultimate product is *trans*-β-chlorostyrene as a result of elimination of HCl from the initially formed *gem*-dichloride and (3) When R is allyl a complex mixture of products is produced.

Satisfied that the protodesilylation is general for 1,1-dihalosilanes, two α-chlorosilanes did react. 1-Chloro-1-trimethylsilylpentane did not react with aqueous sodium hydroxide (entry 10) but 1-chloro-1-trimethylsilyl-2-phenylethane gave styrene in 99% yield (entry 11). That the styrene does not arise from loss of HCl followed by protodesilylation of α-trimethylsilylstyrene was shown by the fact that this olefin is stable to the reaction conditions. It is, therefore, more likely that protodesilylation proceeds in this case followed by loss of HCl.

Other functional organosilanes also undergo protodesilylation. Entries 13, 14 and 15 in Table 1 illustrates that the benzyl, ethynyl and enol silanes all undergo protodesilylation under phase transfer conditions. The allylsilane, 3-trimethylsilylcyclohexene and t-butyldimethylsilyl ethers are stable to these reaction conditions, however.

The protodesilylation of 1,1-dibromo-1-(trimethylsilyl)hexane is representative. A 15 ml round-bottomed flask was charged with 1.0 g (3.16 mmol) of the silane, a small amount of tetra-n-butylammonium bisulfate and 5 ml of 50% aqueous sodium hydroxide at 0°C. The ice-water bath was removed and the solution stirred at room temperature for 3 h. The aqueous layer was extracted with pentane, dried ($CaCl_2$) and concentrated. Fractional distillation gave 0.38 g (49%) of 1,1-dibromohexane, b.p. 178—180°C, n_D^{20} 1.4911 (lit. [5] 1.4914).

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