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VICINAL DEHYDROBROMINATION OF (α-BROMOVINYL)CHLOROSILANES WITH QUINOLINE. A NEW ROUTE TO ETHYNYLCHLOROSILANES

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(α-Bromovinyl)chlorosilanes of the type $CH_2{=}CBrSiR_nCl_{3-n}$ (R = Me, Et; n = 0, 1, 2) were found to be dehydrobrominated with quinoline yielding the corresponding ethynylchlorosilanes.

Vicinal dehydrobromination of haloalkylsilanes to give alkenylsilanes has been well documented and found much synthetic application.[1,2] However, the corresponding elimination of α- or β-bromoalkenylsilanes leading to alkynylsilanes is entirely uncommon. Recently, Cunico and Dexheimer reported that potassium flouride in dimethyl sulfoxide effects the smooth β-elimination of both cis- and trans-β-chlorovinyltrimethylsilane yielding acetylene (eq. 1).[3] In this instance, the reaction involves the loss of the chlorine and trimethylsilyl groups and it has been mentioned that dehydrochlorination is not a favorable process.[3]

$$\left.\begin{array}{l}\text{trans-CHCl=CHSiMe}_3 + \text{KF}\\ \text{cis-CHCl=CHSiMe}_3 + \text{KF}\end{array}\right\rangle \longrightarrow \text{CH}\equiv\text{CH} + \text{Me}_3\text{SiF} + \text{KCl} \qquad (1)$$

We report here the first example of vicinal dehydrobromination of (α-bromovinyl)chlorosilanes effected by quinoline to give ethynylchlorosilanes in fairly good yields (eq. 2).

$$CH_2{=}CBrSiR_nCl_{3-n} + C_9H_7N \longrightarrow CH{\equiv}CSiR_nCl_{3-n} + C_9H_7N{\cdot}HBr \qquad (2)$$

$$(R = Me, Et;\ n = 0, 1, 2)$$

Inspection of Table 1 shows that yields of ethynyldialkylsilanes are satisfactory. Replacement of the chlorine atom for the alkyl group of (α-bromovinyl)dialkylsilanes resulted in decreasing yields of the desired silylacetylenes.

Table 1. Vicinal Dehydrobromination of (α-Bromovinyl)chlorosilanes with Quinoline[a]

Vinylsilane	Ethynylsilane obtained[b]	Yield, %[c]
CH_2=$CBrSiMe_2Cl$	$CH\equiv CSiMe_2Cl$[d]	77
CH_2=$CBrSiEt_2Cl$	$CH\equiv CSiEt_2Cl$[e]	56
CH_2=$CBrSiMeCl_2$	$CH\equiv CSiMeCl_2$[f]	46
CH_2=$CBrSiEtCl_2$	$CH\equiv CSiEtCl_2$[g]	36
CH_2=$CBrSiCl_3$	$CH\equiv CSiCl_3$[h]	10

[a] Reactions were carried out by heating a mixture of an (α-bromovinyl)chlorosilane and quinoline (molar ratio 1/1-1/1.5) at 180-200°C for 15-24 h. [b] IR and NMR spectra showed expected patterns for the structures assigned; see ref. 4. [c] Yields (via GLC) are based on the (α-bromovinyl)chlorosilane charged. [d] $Me_2SiBrCl$ was also obtained in 1% yield. [e] $Et_2SiBrCl$ was also obtained in 1% yield. [f] $MeSiBrCl_2$ was also produced in 39% yield. [g] $EtSiBrCl_2$ was also produced in 21% yield. [h] $SiBrCl_3$ was also formed in 68% yield.

Instead, the formation of compounds of the type $R_nSiBrCl_{3-n}$ (R = Me, Et; n = 0, 1, 2) became increasingly important. For the formation of these undesired products, at least two mechanisms are possible; (a) geminal dehydrobromination of the bromovinylsilanes via the nucleophilic attack by bromide ion followed by rearrangement to acetylene and (b) vicinal dehydrobromination to silylacetylenes followed by desilylation. The mechanism a is not likely since bromide ion-assisted geminal dehalosilylation is not known while fluoride ion effects the reaction.[5] The second possibility was tested by a control experiment which disclosed that ethynylmethyldichlorosilane was cleaved by the hydrogen bromide salt of quinoline to give methylbromodichlorosilane and acetylene.[6] Similar cleavage of CH_2=$CClSiCl_3$ and CHBr=$CBrSiCl_3$ by OH^- is known[7] and consequently, the formation of bromosilanes is not due to the primary process but can be ascribed to the secondary reaction. This assumption was supported by the fact that better yields were obtained by removing ethynylsilanes formed from the system by continuous distillation. Seperate experiments showed that rates for the desilylation fall in the order $CH{\equiv}CSiCl_3 > CH{\equiv}CSiRCl_2 > CH{\equiv}CSiR_2Cl$ while those of vicinal dehydrobromination in the order $CH_2{=}CBrSiCl_3 > CH_2{=}CBrSiRCl_2 > CH_2{=}CBrSiR_2Cl$. Results listed in Table 1 seem to reflect the compromise of the two sets of the reactions.

In spite of such limitations, the present reaction may provide a workable route to ethynylchlorosilanes which have received a growing interest in synthetic and polymer chemistries as important intermediates.[8,9] To date, three methods have been reported for the synthesis of ethynylchlorosilanes, but all of these procedures have some severe disadvantages. For instance, the reaction between hydrosilanes (e.g., $MeSiHCl_2$ and $SiHCl_3$, etc) and 1,2-dichloroethylene requires drastic conditions (i.e., 575°C, 9 h).[10] Zinc-promoted reactions between dimethylchlorosilane and 1,1,2-trichloroethylene must employ expensive solvents such as HMPA to promote the reaction.[9] The reaction of polychlorosilanes with sodium acetylide gives diethynylchlorosilanes (10-25% yields) in addition to the desired ethynylchlorosilanes (10-25% yields).[11]

Further, it should be noted that the simplicity of the procedures for conducting the reaction and work-up permitted a large-scale production of ethynyldimethylchlorosilane and ethynylmethyldichlorosilane in isolated yields of 65 and 34%, respectively, using one mole quantity of the corresponding (α-bromovinyl)methylchlorosilanes.

The following procedure is typical; a mixture of (α-bromovinyl)dimethylchlorosilane (7.0 g, 35 mmol) and quinoline (5.1 g, 39 mmol) was heated at 180-200°C with stirring in a flask equipped with a Vigreux column. The resulting ethynylsilane was gradually distilled out. After 20 h, the reaction reached completion and gave a 98:2 mixture of ethynyldimethylchlorosilane and dimethylbromochlorosilane in 78% yield (3.2 g). The structural assignment for the ethynylchlorosilane was established by its elemental analysis, and IR and NMR spectra. Anal. Found: C, 40.69; H, 6.23. Calcd for C_4H_7ClSi: C, 40.49; H, 5.94. IR (KBr) 3290 [ν(C≡C-H)], 2050 [ν(C≡C)], and 1260 cm^{-1}[δ(SiMe)]; NMR (CCl_4) δ 0.56 (s, 6H, SiMe) and 2.50 (s, 1H, CH≡C).

Work is in progress to explore the scope of the present method.

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6. Ethynylmethyldichlorosilane was found to be stable to quinoline for at least 24 h at 180-190°C. However, we found that this ethynylsilane was cleaved by the hydrogen bromide salt of quinoline. In fact, the treatment of the ethynylsilane with 2-3 equiv. of the salt at 180-190°C for 15 h led to the almost complete conversion of the starting silane into methylbromodichlorosilane and acetylene. It was, however, further found that similar treatment of ethynyldimethylchlorosilane resulted in little occurrence of cleavage.

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