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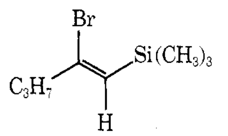
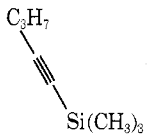
Addition of Hydrogen Bromide to 1-Trimethylsilyl-1-alkynes. A Convenient Synthesis of 2-Bromo-1-alkenes

Summary: The reaction of anhydrous HBr with terminal trimethylsilylalkynes is a rapid free-radical reaction resulting in the elimination of the trimethylsilyl group as the halide and the production of 2-bromo-1-alkenes in high yield; a series of alkynes were studied and some mechanistic details elucidated; the method represents a significant improvement in the synthesis of 2-bromo-1-olefins over existing literature methods.

Sir: For the purposes of other synthetic work, we required a method for the preparation of several isomeric substituted bromovinylsilanes (*e.g.*, β-bromo isomer **1**). One approach to the synthesis of **1** was the addition of hydrogen bromide to **2** in the presence of free-radical initiators like benzoyl peroxide. Previous workers had documented the free-radical addition of hydrogen bromide to trimethylsilylacetylene itself.[1] However, upon exposure of **2**, prepared from lithio-1-pentyne[2] and trimethylsilyl chloride, to excess anhydrous hydrogen bromide under conditions similar to those previously used, no products of the volatility expected for **1** were isolated. On closer examination, the major product was identified as 2-bromo-1-pentene (**3**).[3] This curious result led us to investigate this process further.



1



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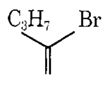
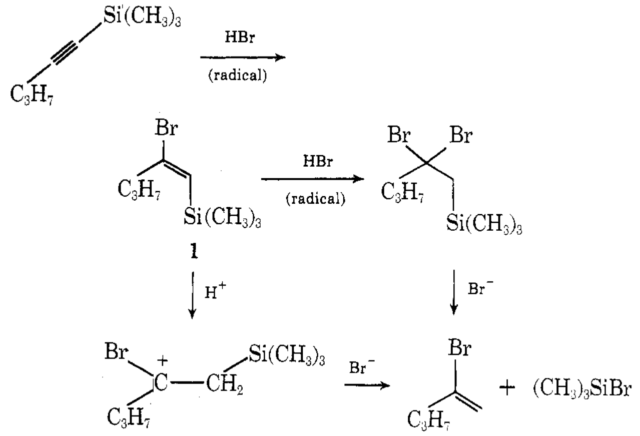


3

Addition of hydrogen bromide to terminal acetylenes is known to produce exclusively 1-bromo-1-alkenes, along with varying amounts of 1,2-dibrominated material.[4] Ionic addition, while extremely sluggish, leads to the 2-bromo isomer in poor yield as well as other dibrominated materials.[5] The apparent rapidity of the reaction with **2** suggested that a radical mechanism was involved.

When the total reaction mixture was examined, another substance produced in about the same amount as the bromo olefin was isolated and identified as trimethylsilyl bromide. We were led to postulate the mechanism shown in Scheme I. The first step of this mechanism is supported by the following data: (1) no addition occurs with anhydrous hydrogen chloride;[6] (2) addition of 2,6-di-*tert*-butyl-4-methylphenol (BHT), a known radical inhibitor, results in complete inhibition of the reaction with hydrogen bromide; (3) under carefully controlled conditions up to 60% of the mono addition product (**1**) can be isolated; (4) as mentioned above the expected stoichiometric quantities of trimethylsilyl bromide were isolated.

Scheme I

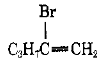
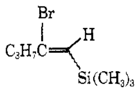
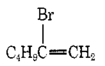
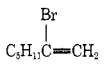
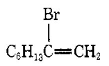
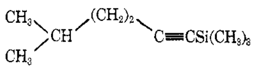
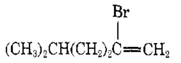
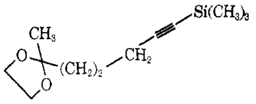
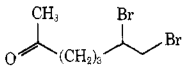
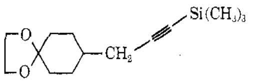
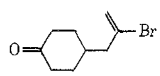
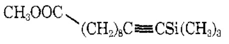
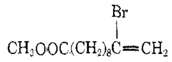


There are two likely mechanistic pathways for the second (and succeeding) step(s) from bromovinylsilane (**1**), ionic or radical as shown. We have established that **1** is transformed by hydrogen bromide to 2-bromoolefin with high efficiency. Our efforts to inhibit this very rapid conversion have been unsuccessful. However, the transformation does not occur upon treatment with anhydrous hydrogen chloride contrary to expectation if the reaction were proceeding by an ionic pathway. While we cannot absolutely rule out an ionic pathway, the radical pathway seems most likely. The final β elimination of trimethylsilyl halides is well documented[7] and has been used recently in a synthesis of 1-bromo olefins.[8] Although β eliminations of this type usually proceed *via* an ionic pathway, there is no evidence to preclude a radical or thermal pathway.[7]

Since a search of the literature led us to the conclusion that few viable synthetic routes to functionalized 2-bromo-1-alkenes exist,[5,9] we subjected a representative series of trialkylsilylacetylenes to anhydrous acid treatment as previously described. The results may be found in Table I.

It was found on a preparative scale that reactions may be run neat at 0° if the acetylene is a liquid, in solvents such as pentane and hexane (reaction rate is reduced), and in

Table I

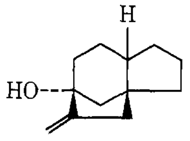
Acetylene[a]	Halo olefin[b]	% yield (isolated)
$C_3H_7C{\equiv}CSi(CH_3)_3$	 $C_3H_7C(Br){=}CH_2$	85[c]
		60[d]
$C_4H_9C{\equiv}CSi(CH_3)_3$	 $C_4H_9C(Br){=}CH_2$	94[c]
$C_5H_{11}C{\equiv}CSi(CH_3)_3$	 $C_5H_{11}C(Br){=}CH_2$	90
$C_6H_{13}C{\equiv}CSi(CH_3)_3$	 $C_6H_{13}C(Br){=}CH_2$	80
	 $(CH_3)_2CH(CH_2)_2C(Br){=}CH_2$	76
 **5**		66
 **6**	 **7**	83
	 $CH_3OOC(CH_2)_8C(Br){=}CH_2$	61

[a] Prepared from commercially available acetylenes. 6 was prepared from cyclohexane-1,3-dione by straightforward methods. [b] Identified by comparison with authentic samples or by comparison of reported literature data. All compounds had consistent ir and nmr spectra and new compounds had acceptable elemental analyses. [c] Yields were determined by vpc (6 ft, 5% SE-30 at 25-75°) by comparison with an internal standard (the appropriate *n*-alkane). [d] Reaction conducted in pentane at 0°, with hydrogen bromide; addition terminated when product formation was at maximum (monitored by vpc). The remainder were treated with hydrogen bromide at 0° for 15-30 min neat or as pentane solutions.

the absence of any peroxide initiators. The presence of peroxides is not required, and in fact is somewhat deleterious, in that the peroxide induces further addition to the 2-bromo olefins leading to 1,2-dibromoalkanes.[4]

This reaction has the possibility of being feasible for the large-scale production of 2-bromo olefins since the expensive trialkylsilyl halide may be nearly quantitatively recovered and recycled. The net conversion then requires only a base and anhydrous hydrogen bromide, and the yields are quite high.

Since trialkylsilylacetylenes are inert to aqueous mineral acids and anhydrous hydrogen chloride, as well as to certain reducing conditions,[10] the halo olefin can be produced when required without the restriction of acid sensitivity in the precursor. Facile removal of ketals occurs under the conditions leading to bromo vinyl ketones as is indicated by the latter entries in Table I. Vinyl halides such as these have found use in the synthesis of polycyclic compounds such as **4** by treatment with lithium dibutylcuprate.[11] An apparent limitation upon the method was encountered when trimethylsilyl-6-heptyn-2-one ethylene ketal (**5**) was utilized. We were unable to control the addition which led exclusively to 6,7-dibromo-2-heptanone. Conceivably, participation of the carbonyl oxygen in an assisted addition is responsible for the observed result. This conclusion is corroborated by the successful conversion of **6** to **7** where intramolecular participation is not possible.



4

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(3) An authentic sample was prepared by literature methods from ethylmagnesium bromide and 2,3-dibromopropene.

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