Halogenation of alkynes and alkynylsilanes

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(Received January 11th, 1989)

Abstract

Halogenation of alkynes has given 1,2-dihalogenoalkenes in good yields. Bromination of alkynylsilanes has given 1,2-dibromovinylsilanes, and reactions with iodine chloride mainly iodoalkynes.

Introduction

The halogenation of alkynes has not been much studied. The bromination to form a trans dibromide is catalyzed by bromide ion and has been suggested to take place via nucleophilic addition; the proportion of product formed by trans addition is higher in the presence of an excess of bromide ion [1,2]. Stereochemistry was established by measurement of dipole moments [3].

Recently we described a new method for preparing 1-halogeno-1-(trimethylsilyl)-2,2-dialkyl olefins [4], which are useful for preparing substituted olefins [5]. The 1,2-dihalogeno olefins have not so far been much used in synthesis, but we thought it that the availability of mixed 1,2-dihalogeno olefins would open new routes to substituted olefins and this prompted us to search for convenient procedures for their synthesis.

We describe here a further study of halogenation of alkynes, with emphasis on the synthesis of 1,2-dibromovinylsilanes, which have been made for the first time.

Results and discussion

First, we reinvestigated the bromination of diphenylacetylene (1), and obtained a 95% yield of the corresponding dibromide (2). Use of 2 equivalents of bromine did not lead to formation of the tetrabromide under the conditions used (−12°C). Under the same conditions treatment of diphenylacetylene with chlorine gave a 50% yield of the corresponding dichloro compound (3).

Iodation of diphenylacetylene was very slow and after 48 h at room temperature
with an excess of iodine gave only 20% of the diiodide (4) leaving 80% of starting material (1). Increase in the reaction temperature did not raise the yield.

Reaction of diphenylacetylene with iodine chloride gave a 90% yield of the chloroiodo compound (5), but reaction with iodine bromide gave only a 30% yield of the bromo-iodo compound (6).

There was no reaction with N-bromosuccinimide or N-chlorosuccinimide under various reaction conditions. This is consistent with the fact that such halogenation is activated by halide ion and takes place via nucleophilic addition [1,2].

Our attempts to bring about alkylation [6] of these dihalo compounds (using alkyllithium followed by alkyl iodide) or coupling involving organocuprates [6] or Pd catalyst and arylmetals [7], all led to diphenylacetylene, implying that elimination is a facile process. However, the dihalides can still be used in Diels–Alder reactions or in the synthesis of some organic compounds [8].

Halogenation of alkylnylsilanes was investigated here for the first time. It was found that bromination of various alkylnylsilanes with 1.2 equivalents of bromine in carbon tetrachloride at −12°C for 0.5 h gave good to fair yields of the corresponding dibromides.

\[
\text{R} \equiv \text{CSiMe}_3 \xrightarrow{1.2 \text{ equiv. Br}_2/\text{CCl}_4, -12^\circ \text{C}/0.5 \text{ h}} \quad \text{R} \equiv \text{Br} \equiv \text{SiMe}_3
\]

\[(7)\]

<table>
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<tr>
<th>R</th>
<th>Ph</th>
<th>Me$_3$Si</th>
<th>H</th>
<th>Me</th>
<th>Cyclohexyl</th>
<th>n-Bu</th>
<th>HOCH$_2$</th>
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<tr>
<td>% yield</td>
<td>82</td>
<td>42</td>
<td>57</td>
<td>60</td>
<td>56</td>
<td>61</td>
<td>53</td>
</tr>
</tbody>
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Treatment of these dibromovinylsilanes (8) with alkyllithium followed by alkyl iodide [6] led only to bromoalkynes (9).

\[
\text{Br} \equiv \text{SiMe}_3 \xrightarrow{1. \text{ BuLi}, 2. \text{ CH}_3} \quad \text{R} \equiv \text{CBr}
\]

\[(9)\]

Treatment of bis(trimethylsilyl)acetylene (10) with iodine monochloride in carbon tetrachloride at −12°C for 0.5 hour gave iodoethynyltrimethylsilane (11) as a major product along with unidentified side products. Reaction at room temperature gave a 90% yield of iodoethynyltrimethylsilane (10) with fewer side products. This suggests that electrophilic substitution takes place, as is usual with alkylnylsilanes [9]. However, an attempt to use iodine monobromide, in the same way gave only a mixture of unidentified products.

\[
\text{Me}_3\text{SiC} \equiv \text{SiMe}_3 \xrightarrow{1.2 \text{ equiv. ICl/CCl}_4, \text{roomtemp./2 h}} \quad \text{Me}_3\text{SiC} \equiv \text{Cl}
\]

\[(10)\] \[(11, 90\%)\]

**Experimental**

**Spectra.** Unless otherwise indicated the $^1$H NMR data refer to solutions in CDCl$_3$ with internal CHCl$_3$ as reference.

1,2-Dibromo-1,2-diphenylethene (2). To 1.78 g (10 mmol) of diphenylacetylene in 20 ml of CCl$_4$ at −12°C was added dropwise 12 ml of 1M solution of bromine in
CCl₄ (1.2 equiv., 12 mmol) at −12 °C. The reaction mixture was stirred for 0.5 hour then added to 10% aqueous sodium sulfite. After extraction with hexane and drying of the extract over sodium sulfate, the solvent was removed on a rotary evaporator to leave a residue, which was recrystallized from ethanol to give 3.21 g (9.5 mmol, 95% yield) of the desired product as a white crystalline solid: m.p. 210 °C (lit. [10] 209 °C) NMR (internal reference TMS) δ(H): 7.42 ppm (singlet, 10H, phenyl protons). Comparison with an authentic sample [9] gave superimposable spectra and a single peak in GLC (OV1 glass column) upon co-injection.

1-Chloro-2-iodo-1,2-diphenylethene (5). The analogous procedure gave a 90% yield of a white crystalline solid: m.p. 89 °C; NMR (internal reference TMS) δ(H): 7.43 ppm (multiplet, 10H, phenyl protons).

1,2-Dibromo-1-(trimethylsilyl)-2-phenylethene. A similar product but purification of the product by chromatography on silica gel with hexane as eluent gave a 82% yield of colourless product. NMR δ(H): 0.03 (singlet, 9H, (CH₃)₃Si) and 7.36 ppm (singlet, 5H, phenyl protons); mass spectrum, calculated (m/e) for C₁₁H₁₄Br₂Si: 331.9233; found 331.9233.

1,2-Dibromo-1,2-bis(trimethylsilyl)ethene. A procedure analogous to that in the preceding experiment gave a 42% yield of colourless product; NMR δ(H): 0.00 ppm (singlet, 18H, 2(CH₃)₃Si); mass spectrum, calculated (m/e) for C₈H₁₈Br₂Si₂: 327.9314; found 327.9343.

1,2-Dibromo-1-(trimethylsilyl)ethene. This was made similarly in 57% yield: NMR δ(H): 0.24 (singlet, 9H, (CH₃)₃Si) and 7.06 ppm (singlet, 1H, HC=C); high resolution mass spectrum, calculated (m/e) for C₅H₁₀Br₂Si: 255.8918; found: 255.8809.

1,2-Dibromo-1-(trimethylsilyl)-1-propene. This was made similarly in 60% yield; NMR δ(H): 0.25 (singlet, 9H, (CH₃)₃Si) and 2.39 ppm (singlet, 3H, CH₃); mass spectrum, calculated (m/e) for C₅H₁₀Br₂Si: 269.9075; found: 269.9112.

1,2-Dibromo-1-(trimethylsilyl)-2-cyclohexylethene. This was made similarly in 56% yield; NMR δ(H): 0.29 (singlet, 9H, (CH₃)₃Si) and 1.2–2.5 ppm (multiplet, 11H, cyclohexyl protons; mass spectrum, calculated (m/e) for C₁₁H₂₀Br₂Si: 337.9701; found: 337.9718.

1,2-Dibromo-1-(trimethylsilyl)-1-hexene. This was made similarly in 61% yield; NMR δ(H): 0.24 (singlet, 9H, (CH₃)₃Si), 0.96 (multiplet, 3H, CH₃), 1.6 (multiplet, 4H, (CH₂)₂), and 2.7 ppm (triplet, 2H, CH₂C=C J 7 Hz); mass spectrum, calculated (m/e) for C₈H₁₈Br₂Si: 311.9544; found: 311.9532.

1,2-Dibromo-3-(trimethylsilyl)-3-propene-1-ol. A similar procedure but with hexane/dichloromethane (70/30) as eluent gave a 53% yield; NMR δ(H): 0.31 (singlet, 9H, (CH₃)₃Si), 3.8 (singlet 1H, OH) and 4.50 ppm (singlet, 2H, CH₂O); mass spectrum, calculated (m/e) for C₅H₁₂Br₂OSi: 285.9024; found 285.9014.

1-(Trimethylsilyl)-2-iodoethyne (II). In this case the product was distilled at reduced pressure to give a 90% yield liquid b.p. 52 °C/14 mmHg (lit. [10] 53 °C/15 mmHg), δ(H) 0.14 ppm (singlet, 9H, (CH₃)₃Si).

Acknowledgement

I am grateful to the Research Center, College of Science, King Saud University for financial support for this work grant No. (Chem/1403/23). I thank Dr. R.B. Miller of the University of California at Davis for generously allowing use of his
laboratory facilities, including high resolution mass spectrometry. I also thank Mr. M.M. Ahmad for technical assistance.

References