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Halogenation of alkynes and alkynylsilanes

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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 promoted 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**).

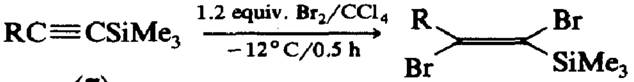
Iodation of diphenylacetylene was very slow and after 48 h at room temperature with an excess of iodine gave only 20% of the diiodide (**4**) leaving 80% of starting material (**1**). Increase in the reaction temperature did not raise the yield.

Reaction of diphenylacetylene with iodine chloride gave a 90% yield of the chloroiodo compound (**5**), but reaction with iodine bromide gave ony 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^0 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 alkynylsilanes was investigated here for the first time. It was found that bromination of various alkynylsilanes 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.

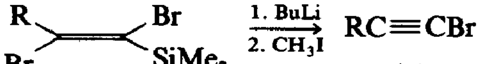


(**7**)

(**8**)

R =	Ph	Me_3Si	H	Me	Cyclohexyl	n-Bu	$HOCH_2$
% yield	82	42	57	60	56	61	53

Treatment of these dibromovinylsilanes (**8**) with alkyllithium followed by alkyl iodide [6] led only to bromoalkynes (**9**).



(**9**)

(**8**)

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 suggest that electrophilic substitution takes place, as is usual with alkynylsilanes [9]. However, an attempt to use iodine monobromide, in the same way gave only a mixture of unidentified products.

$$\underset{(\mathbf{10})}{Me_3SiC{\equiv}SiMe_3} \xrightarrow[\text{roomtemp./2 h}]{\text{1.2 equiv. } ICl/CCl_4} \underset{(\mathbf{11},\ 90\%)}{Me_3SiC{\equiv}CI}$$

Experimental

Spectra. Unless otherwise indicated the ^1H 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 1*M* solution of bromine in

CCl_4 (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, $(CH_3)_3Si$) and 7.36 ppm (singlet, 5H, phenyl protons); mass spectrum, calculated (m/e) for $C_{11}H_{14}{}^{79}Br_2Si$: 331.9231; 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 colorless product; NMR δ(H): 0.00 ppm (singlet, 18H, $2(CH_3)_3Si$); mass spectrum, calculated (m/e) for $C_8H_{18}{}^{79}Br_2Si_2$: 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, $(CH_3)_3Si$) and 7.06 ppm (singlet, 1H, HC=C); high resolution mass spectrum, calculated (m/e) for $C_5H_{10}{}^{79}Br_2Si$: 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, $(CH_3)_3Si$) and 2.39 ppm (singlet, 3H, CH_3); mass spectrum, calculated (m/e) for $C_6H_{12}{}^{79}Br_2Si$: 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, $(CH_3)_3Si$) and 1.2–2.5 ppm (multiplet, 11H, cyclohexyl protons; mass spectrum, calculated (m/e) for $C_{11}H_{20}{}^{79}Br_2Si$: 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, $(CH_3)_3Si$), 0.96 (multiplet, 3H, CH_3), 1.6 (multiplet, 4H, $(CH_2)_2$), and 2.7 ppm (triplet, 2H, $CH_2C{=}C$ J 7 Hz); mass spectrum, calculated (m/e) for $C_9H_{18}{}^{79}Br_2Si$: 311.9544; found: 311.9532.

1,2-Dibromo-3-(trimethylsilyl)-3-propene-1-01. A similar procedure but with hexane/dichloromethane (70/30) as eluent gave a 53% yield; NMR δ(H): 0.31 (singlet, 9H, $(CH_3)_3Si$), 3.8 (singlet 1H, OH) and 4.50 ppm (singlet, 2H, CH_2O); mass spectrum, calculated (m/e) for $C_6H_{12}{}^{79}Br_2OSi$: 285.9024; found 285.9014.

1-(Trimethylsilyl)-2-iodoethyne (11). 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, $(CH_3)_3Si$).

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References

1 J. Konig and V. Wolf, Tetrahedron Lett., (1970) 1629.
2 R. Pettit and J. Henery, Org. Syn., 50 (1970) 36.
3 J.A. Pincock and K. Yates, J. Amer. Chem. Soc., 90 (1968) 5643.
4 R.B. Miller and M.I. Al-Hassan, J. Org. Chem., 49 (1984) 725.
5 R.B. Miller and G. McGarvey, J. Org. Chem., 44 (1979) 4623.
6 R.B. Miller, M.I. Al-Hassan and G. McGarvey, Synth. Commun., 13 (1983) 969.
7 M.I. Al-Hassan, J. Organomet. Chem., 321 (1987) 119.
8 W.C. Kray, J.R., and C.E. Castro, Org. Biolog. Chem., 5 (1964) 4603.
9 T.H. Chan and Ian Feleming, Synthesis, (1979) 761.
10 H. Buchert and W. Zeil, Spectrochim. Acta, 18 (1962) 1043.