Bromination of alkenes and alkynes with (bromodimethyl)sulfonium bromide

Biswanath Das*, Yallamalla Srinivas, Chittaluri Sudhakar and Bommena Ravikanth

Organic Chemistry Division-I, Indian Institute of Chemical Technology, Hyderabad-500 007, India

Alkenes and alkynes were brominated efficiently in high yields with (bromodimethyl)sulfonium bromide in acetonitrile at room temperature. Alkenes produced the corresponding *trans*-dibromo compounds while alkynes (except phenylacetylene) afforded both the *trans*-dibromo products (major) and the tetrabromo derivatives (minor). However, phenylacetylene furnished solely the tetrabromo compound.

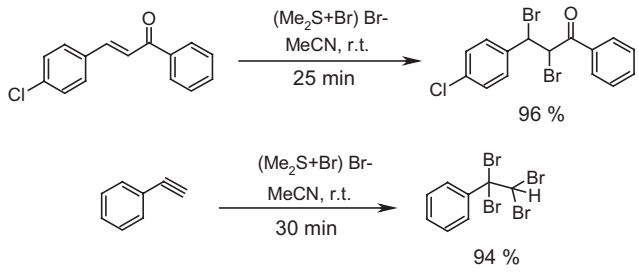
Keywords: alkene, alkyne, (bromodimethyl)sulfonium bromide

The conversion of alkenes and alkynes into their corresponding bromo derivatives is useful in organic synthesis as the bromine can be transformed to various other functional groups.[1] Brominated alkenes are also used for the preparation of organometallic reagents.[2] The bromination of alkenes and alkynes can be accomplished by using hazardous elemental bromine.[1] Some alternative methods for bromination which do not employ bromine directly have also been developed.[1,3-9] However, the cost of the reagents, harsh reaction conditions and unsatisfactory yields due to side reactions, are disadvantages of many of these methods.

In connection with our work[10,11] on the application of (bromodimethyl)sulfonium bromide[12-15] in the development of useful synthetic methodologies we have discovered that this reagent is highly effective for bromination of both alkenes and alkynes (Scheme 1).

A series of alkenes and alkynes were brominated at room temperature in short reaction times (15–30 min) following the above method (Table 1). The products were formed in excellent yields. All the alkenes produced the corresponding vicinal *trans*-dibromo compounds. However, the alkynes (except phenylacetylene) produced both the dibromo (*trans*) and tetrabromo compounds. The dibromo compounds were the major products. Phenylacetylene formed only the tetrabromo product in a yield of 94%. The structures of the bromo compounds were established from their spectral (^{1}H NMR and MS) data.

(Bromodimethyl)sulfonium bromide[12-15] is an inexpensive reagent. Its application has not yet been fully explored. Previously one protocol for the treatment of alkenes with (bromodimethyl)sulfonium bromide at 0°C afforded mainly the corresponding 1-bromo-2-sulfonium bromides along with 1,2-dibromides.[14] Here the reagent has been employed



Scheme 1

efficiently for solely bromination of alkenes and alkynes. The plausible mechanism of the reaction is shown below (Scheme 2).

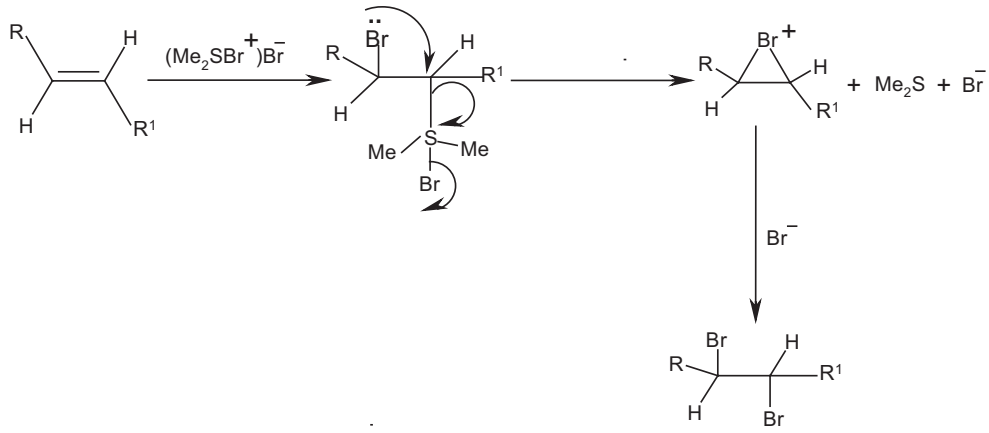
In conclusion, a useful application of (bromodimethyl)sulfonium bromide as an efficient reagent for the bromination of alkenes and alkynes in short reaction times and in excellent yields under mild reaction conditions has been discovered.

Experimental

Melting points were measured on a Büchi 510 instrument and are uncorrected. The spectra were determined with the following instruments: NMR, Varian Gemini 200 MHz and MS: FABMS VG Autospec, Column chromatography was performed over silica gel (BDH, 100-200 mesh) and TLC with silica gel GF_{254}.

General experimental procedure

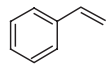
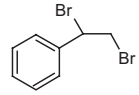
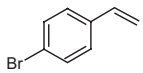
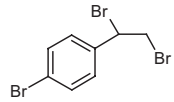
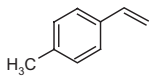
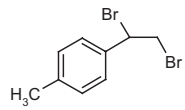
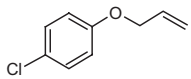
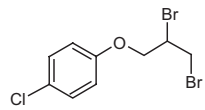
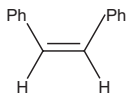
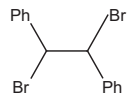
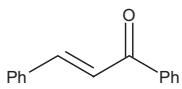
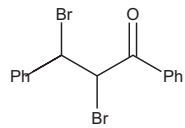
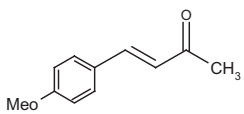
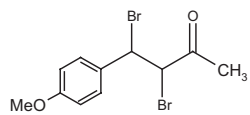
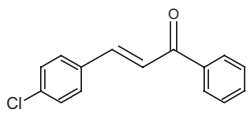
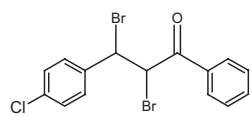
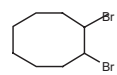
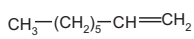
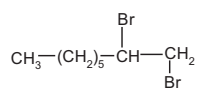
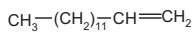
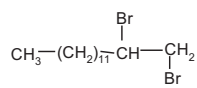
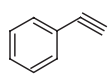
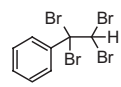
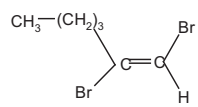
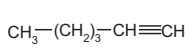
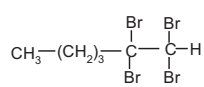
An alkene (0.5 mmol) or alkyne (0.5 mmol) and (bromodimethyl)sulfonium bromide (0.6 mmol) were added to acetonitrile (5 ml). The mixture was stirred at room temperature and the reaction was monitored by TLC. After completion, the solvent was evaporated



Scheme 2

* Correspondent. E-mail: biswanathdas@yahoo.com

Table 1 Preparation of dibromo compounds from alkenes and alkynes using (bromodimethyl) sulfonium bromide

Entry	Substrate	Product[a]	Time/min	Isolated yield/%	M.p. (m.p.)[Lit]/°C
1			15	96	74 (74–76)[8]
2			15	94	56–58
3			15	98	Viscous
4			15	93	Viscous
5			15	95	233–234 (235)[5]
6			25	92	154–155 (156–158)[8]
7			25	94	Viscous
8			25	96	160–161
9			15	95	Colourless oil
10			15	92	Viscous liquid
11			15	91	Viscous
12			30	94	74 (72)[6]
13			30	61	Pale yellow oil
		+ 		29	Viscous

[a]The structures of the products were determined from spectral (^{1}H NMR and MS) data.

under vacuum and water (10 ml) was added. The mixture was extracted with EtOAc (3 × 10 ml) and the extract was dried and concentrated. The crude mass was subjected to column chromatography (silica gel, hexane-EtOAc) to offord the pure dibromo or tetrabromo product.

The spectra (^{1}H NMR and MS) of the unknown bromo compounds are given below.

Compound (**2**): White solid. M.p. 56–58°C. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.55 (d, J = 8.0 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 5.05 (dd,

J = 9.0, 5.0 Hz, 1H), 4.04 (dd, *J* = 12.0, 5.0 Hz, 1H), 3.94 (dd, *J* = 12.0, 9.0 Hz, 1H). FABMS: *m/z* 363, 365, 367, 369 $[M + Na]^+$. Anal. Calcd for $C_8H_7Br_3$: C, 27.99; H, 2.04%. Found: C, 28.19; H, 2.02%.

Compound (**4**): Viscous oil. ^1H NMR ($CDCl_3$, 200 MHz): δ 7.24 (d, *J* = 8.0 Hz, 2H), 6.85 (d, *J* = 8.0 Hz, 2H), 3.85 (d, *J* = 6.0 Hz, 2H), 4.45–4.26 (m, 3H). FABMS: *m/z* 349, 351, 353, 355 $[M + Na]^+$. Anal. Calcd for $C_9H_9OBr_2Cl$: C, 32.88; H, 2.74%. Found: C, 33.12; H, 2.81%.

Compound (**7**): Viscous. ^1H NMR ($CDCl_3$, 200 MHz): δ 7.92 (d, *J* = 8.0 Hz, 2H), 6.94 (d, *J* = 8.0 Hz, 2H), 3.91 (s, 2H), 3.86 (s, 3H), 2.56 (s, 3H). FABMS: *m/z* 357, 359, 361 $[M + Na]^+$. Anal. Calcd for $C_{11}H_{12}O_2Br_2$: C, 39.29; H, 3.57%. Found: C, 39.49; H, 3.57%.

Compound (**8**): White solid. M.p 160–161°C. ^1H NMR ($CDCl_3$, 200 MHz): δ 8.06 (d, *J* = 8.0 Hz, 2H), 7.80–7.30 (m, 7H), 5.71 (d, *J* = 9.0 Hz, 1H), 5.57 (d, *J* = 9.0 Hz, 1H). FABMS: *m/z* 423, 425, 427, 429 $[M + Na]^+$. Anal. Calcd for $C_{15}H_{11}OBr_2Cl$: C, 44.72; H, 2.73%. Found: C, 44.97; H, 2.71%.

Compound (**11**): Viscous. ^1H NMR ($CDCl_3$, 200 MHz): δ 4.13 (m, 1H), 3.84 (dd, *J* = 12.0, 4.0 Hz, 1H), 3.57 (dd, *J* = 12.0, 10.0 Hz, 1H), 2.15 (m, 1H), 1.76 (m, 1H), 1.64–1.20 (m, 20H), 0.88 (t, *J* = 7.0 Hz, 3H). FABMS: *m/z* 377, 379, 381 $[M + Na]^+$. Anal. Calcd for $C_{14}H_{28}Br_2$: C, 47.19; H, 7.87%. Found: C, 47.51; H, 7.88%.

Compound (**13**). Viscous. ^1H NMR (200 MHz, $CDCl_3$): δ 4.16 (s, 1H), 2.65 (t, *J* = 7.0 Hz, 2H), 1.72–1.64 (m, 2H), 1.42–1.23 (m, 2H), 0.96 (t, *J* = 7.0 Hz, 3H). FABMS: *m/z* 421, 423, 425, 427, 429 $[M + Na]^+$. Anal. Calcd for $C_6H_{10}Br_4$: C, 17.91; H, 2.49%. Found: C, 18.14; H, 2.57%.

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