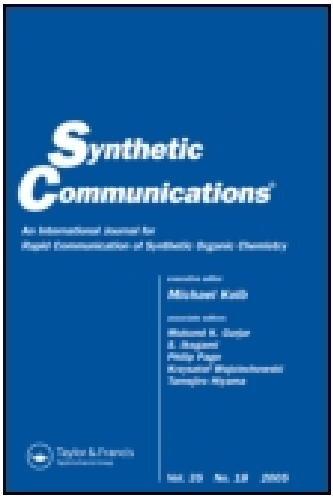


Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Efficient Bromination of Alkenes and Alkynes Using Potassium Bromide and Diacetoxy Iodobenzene

Biswanath Das [a], Yallamalla Srinivas [a], Chittaluri Sudhakar [a], Kongara Damodar [a] & Ravirala Narender [a]

[a] Organic Chemistry Division I, Indian Institute of Chemical Technology, Hyderabad, Andhra Pradesh, India

Published online: 22 Dec 2008.

To cite this article: Biswanath Das, Yallamalla Srinivas, Chittaluri Sudhakar, Kongara Damodar & Ravirala Narender (2008) Efficient Bromination of Alkenes and Alkynes Using Potassium Bromide and Diacetoxy Iodobenzene, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 39:2, 220-227, DOI: 10.1080/00397910801979379

To link to this article: http://dx.doi.org/10.1080/00397910801979379

Synthetic Communications®, 39: 220–227, 2009

ISSN: 0039-7911 print/1532-2432 online
DOI: 10.1080/00397910801979379

Taylor & Francis
Taylor & Francis Group

Efficient Bromination of Alkenes and Alkynes Using Potassium Bromide and Diacetoxy Iodobenzene

Biswanath Das, Yallamalla Srinivas, Chittaluri Sudhakar, Kongara Damodar, and Ravirala Narender
Organic Chemistry Division I, Indian Institute of Chemical Technology, Hyderabad, Andhra Pradesh, India

Abstract: Bromination of alkenes and alkynes has efficiently been carried out at room temperature in short reaction times using KBr and diacetoxy iodobenzene in CH_2Cl_2-H_2O (1:1) to prepare the corresponding *trans*-dibromo compounds in excellent yields.

Keywords: Alkene, alkyne, DIB, *trans*-dibromo compound

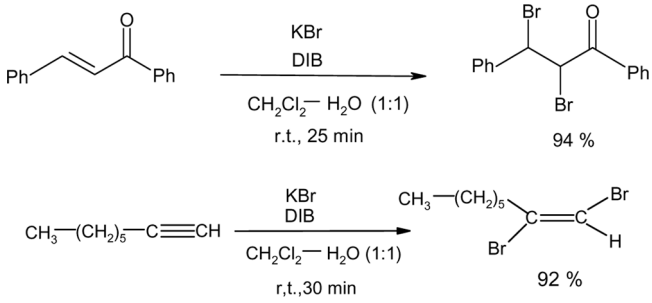
The bromination of alkenes and alkynes is an important transformation in organic synthesis.[1] The protection and deprotection of double bonds via a bromination–debromination strategy can conveniently be utilized in synthetic routes.[2] The bromine group can also easily be converted into other functionalities.[1] Additionally, the brominated alkenes are useful precursors to organometallic reagents.[3] The classical bromination involves the use of hazardous elemental bromine.[1] To avoid this reagent, several other protocols for bromination have been discovered.[4–10] However, the occurrence of side reactions, low selectivity, poor yields, and application of costly reagents are drawbacks in several methods. Here we report an efficient method for bromination of alkenes and alkynes.

In continuation of our work[11–13] on the development of useful synthetic methodologies, we have observed that the bromination of alkenes

Received December 22, 2007.

Part 158 in the series, "Studies on Novel Synthetic Methodologies."

Address correspondence to B. Das, Organic Chemistry Division I, Indian Institute of Chemical Technology, Uppal Road, Hyderabad 500 007, Andhra Pradesh, India. E-mail: biswanathdas@yahoo.com



Scheme 1. Bromination of alkenes and alkynes using KBr and diacetoxy iodobenzene.

and alkynes to the corresponding vicinal dibromo compounds can easily be carried out using KBr and diacetoxy iodobenzene (DIB) in CH_2Cl_2-H_2O (1:1) (Scheme 1).

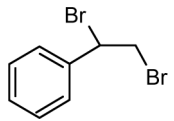
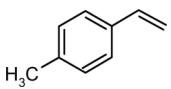
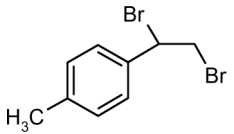
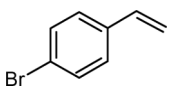
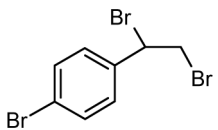
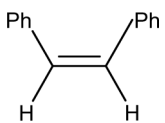
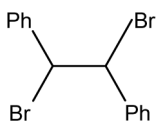
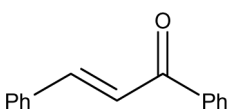
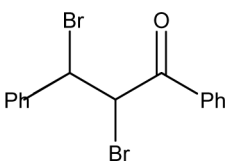
In recent years, hypervalent iodine reagents have gained much importance in organic synthesis because of their interesting activity, ready availability, and easy handling.[14,15] Previously we applied DIB to the preparation of isoxazolines from activated alkenes by treatment with aldoximes.[16] We have now discovered that this reagent in combination with KBr is highly effective for bromination of various alkenes and alkynes (Table 1). α,β- Unsaturated carbonyl compounds and cycloalkenes were also efficiently brominated.

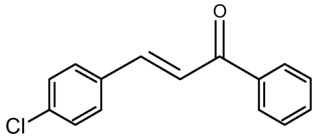
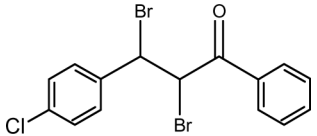
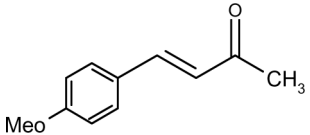
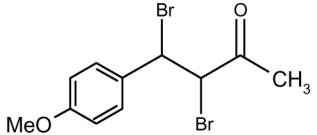
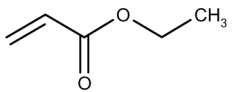
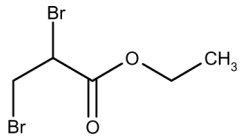
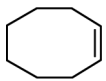
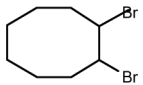
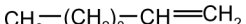
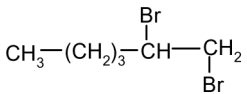
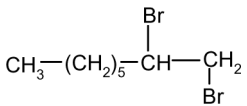
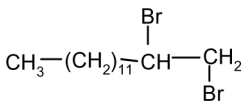
The conversion occurred at room temperature under mild reaction conditions. The reaction was complete within 15–30 min and the yields were excellent (92–98%). CH_2Cl_2-H_2O (1:1) was found to be a suitable medium for this conversion.

The bromination of alkenes and alkynes (except phenyl acetylene) produced solely the *trans*-vicinal dibromo compounds. Phenyl acetylene afforded the corresponding *trans*-(E)-dibromo derivative as the major product (84%) along with the *cis*-(Z)-dibromo compound in minor quantity (12%). The bromonium ion (Br^+) generated in situ by the reaction of KBr and DIB reacts with the alkene or alkyne to form a cyclic bromonium ion intermediate, which is attacked by a bromide ion from the reverse side, forming selectively the *trans*-vicinal dibromo compound. No tetrabromo derivatives were obtained from alkynes.

In conclusion, we have developed a simple, novel, mild, and efficient method for high-yielding preparation of vicinal *trans*-dibromo compounds from alkenes and alkynes by treatment with a combination of KBr and DIB. The molecular bromine that is toxic can thus be avoided. A new synthetic utility of hypervalent iodine has also been disclosed.

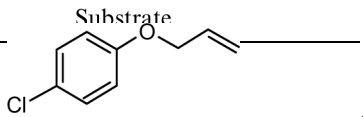
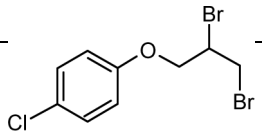
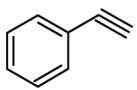
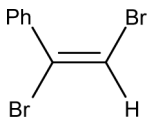
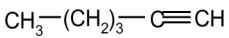
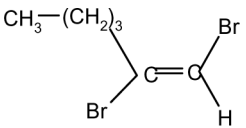
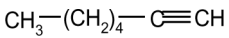
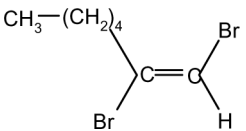
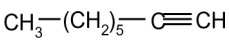
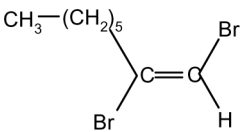
Table 1. Preparation of dibromo compounds from alkenes and alkynes using DIB and KBr

Entry	Substrate	Product[a]	Time (min)	Isolated yield (%)	Reference
1			15	97	9
2			15	98	9
3			15	96	—
4			15	98	6
5			25	94	9

6			25	95	—
7			25	96	—
8			20	93	—
9			15	97	7
10			15	94	9
11			15	93	9
12			15	95	—

(*Continued*)

Table 1. Continued

Entry	Substrate		Time (min)	Isolated yield (%)	Reference
13			15	96	—
14			30	84	9
15			30	94	7
16			30	93	—
17			30	92	9

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

EXPERIMENTAL

General

A mixture of alkene or alkyne (0.5 mmol), KBr (1.5 mmol), and DIB (0.5 mmol) in CH_2Cl_2-H_2O (1:1) (5 mL) was stirred at room temperature. The reaction was monitored by thin-layer chromatography (TLC). After completion, the organic layer was separated, washed with saturated aqueous $NaHCO_3$ solution (3×5 mL), and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure. The residue was subjected to column chromatography (silica gel, hexane–EtOAc) to obtain pure dibromo product.

The spectral (^{1}H NMR and MS) and analytical data of some representative dibromo compounds are given next.

Data

1,2-Dibromo-1-(4-bromo)-1-phenylethane (Table 1, entry 3)

White solid, mp 56–58°C. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.55 (d, 2H, $J = 8.0$ Hz), 7.35 (d, 2H, $J = 8.0$ Hz), 5.05 (dd, 1H, $J = 9.0$, 5.0 Hz), 4.04 (dd, 1H, $J = 12.0$, 5.0 Hz), 3.94 (dd, 1H, $J = 12.0$, 9.0 Hz); FABMS: m/z 363, 365, 367, 369 $[M + Na]^+$. Anal. calcd. for $C_8H_7Br_3$: C, 28.23; H, 2.06. Found: C, 27.87; H, 1.98.

2,3-Dibromo-1-phenyl-3-(4-chloro)-phenyl propane-1-one
(Table 1, entry 6)

White solid, mp 160–161°C. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 8.06 (d, 2H, $J = 8.0$ Hz), 7.80–7.30 (m, 7H), 5.71 (d, 1H, $J = 9.0$ Hz), 5.57 (d, 1H, $J = 9.0$ Hz); FABMS: m/z 423, 425, 427, 429 $[M + Na]^+$. Anal. calcd. for $C_{15}H_{11}OBr_2Cl$: C, 44.94; H, 2.75. Found: C, 43.64; H, 2.67.

2,3-Dibromo-3-(4-methoxy)-phenyl-methyl propanoate
(Table 1, entry 7)

Viscous, ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.92 (d, 2H, $J = 8.0$ Hz), 6.94 (d, 2H, $J = 8.0$ Hz), 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, 39.52; H, 3.59. Found: C, 38.49; H, 3.51.

2,3-Dibromo-ethyl propanoate (Table 1, entry 8)

Viscous, ^{1}H NMR ($CDCl_3$, 200 MHz): δ 4.36 (dd, 1H, $J = 10.0$, 4.0 Hz), 4.30 (q, 2H, $J = 7.0$ Hz), 3.92 (dd, 1H, $J = 12.0$, 10.0 Hz), 3.66 (dd, 1H, $J = 12.0$, 4.0 Hz), 1.36 (t, 3H, $J = 7.0$ Hz); FABMS: m/z 281, 283, 285 $[M + Na]^+$. Anal. calcd. for $C_5H_8O_2Br_2$: C, 23.25; H, 3.10. Found: C, 22.09; H, 3.16.

1,2-Dibromo-tetradecane (Table 1, entry 12)

Viscous, ^{1}H NMR ($CDCl_3$, 200 MHz): δ 4.13 (m, 1H), 3.84 (dd, 1H, $J = 12.0$, 4.0 Hz), 3.57 (dd, 1H, $J = 12.0$, 10.0 Hz), 2.15 (m, 1H), 1.76 (m, 1H), 1.64–1.20 (m, 20H), 0.88 (t, 3H, $J = 7.0$ Hz); FABMS: m/z 377, 379, 381 $[M + Na]^+$. Anal. calcd. for $C_{14}H_{28}Br_2$: C, 47.46; H, 7.91. Found: C, 46.34; H, 7.84.

2,3-Dibromo-propyl-(4-chloro)-phenyl-ether (Table 1, entry 13)

Viscous, ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.24 (d, 2H, $J = 8.0$ Hz), 6.85 (d, 2H, $J = 8.0$ Hz), 3.85 (d, 2H, $J = 6.0$ Hz), 4.45–4.26 (m, 3H); FABMS: m/z 349, 351, 353, 355 $[M + Na]^+$. Anal. calcd. for $C_9H_9OBr_2Cl$: C, 33.08; H, 2.76. Found: C, 32.83; H, 2.82.

1,2-Dibromo-1-heptene (Table 1, entry 15)

Viscous, ^{1}H NMR ($CDCl_3$, 200 MHz): δ 6.39 (s, 1H), 2.60 (t, 2H, $J = 7.0$ Hz), 1.63–1.51 (m, 2H), 1.40–1.23 (m, 4H), 0.88 (t, 3H, $J = 7.0$ Hz); FABMS: m/z 277, 279, 281 $[M + Na]^+$. Anal. calcd. for $C_7H_{12}Br_2$: C, 33.07; H, 4.72. Found: C, 31.96; H, 4.66.

ACKNOWLEDGMENTS

The authors thank Council of Scientific and Industrial Research and University Grants Commission, New Delhi, for financial assistance.

REFERENCES

1. House, H. O. *Modern Synthetic Reactions*, 2nd ed.; W. A. Benjamin Inc., Menlo Park, CA, 1972; p. 422.
2. Ranu, B. C.; Guchhait, S. K.; Sarkar, A. Stereoselective debromination of aryl-substituted vic-dibromide with indium metal. *Chem. Commun.* **1998**, 2113.

3. Rieke, R. D.; Sell, M. S. In *Handbook of Grignard Reagents*; G. S. Silverman and P. E. M. Rakita (Eds.); Dekker: New York, 1996; Chap. 26, p. 527.
4. Fieser, L. F.; Fieser, M. *Reagents for Organic Synyhesis*; Wiley: New York, 1967: Vol. 1, p. 967.
5. Berthelot, J.; Benammar, Y.; Lange, C. A mild and efficient sonochemical bromination of alkenes using tetrabutylammonium tribromide. *Tetrahedron Lett*. **1991**, *32*, 4135.
6. Hazra, G.; Chordia, M. D.; Bahule, B. B.; Pore, V. S.; Basu, S. Manganese-mediated novel dibromination of olefins with tetradecyltrimethylammonium permanganate and trimethylbromosilane. *J. Chem. Soc., Perkin Trans.* 1, **1994**, 1667.
7. Barhate, N. B.; Gaajare, A. S.; Wakharkar, R. D.; Bedekar, A. V. Simple and practical halogenation of arenes, alkenes, and alkynes with hydrohalic acid-/H_2O_2 (or TBHP). *Tetrahedron* **1999**, *55*, 11127.
8. Rodebaugh, R.; Dahenham, J. S.; Fraser-Reid, B.; Snyder, J. P. Bromination of alkenyl glycosides with copper(II) bromide and lithium bromide: Synthesis, mechanism, and DFT calculations. *J. Org. Chem*, **1999**, *64*, 1758.
9. Nair, V.; Panicker, S. B.; Augustine A.; George, T. G.; Thomas, S.; Vairamani, M. An efficient bromination of alkenes using cerium(IV) ammonium nitrate (CAN) and potassium bromide. *Tetrahedron* **2001**, *57*, 7417.
10. Moriuchi, T.; Yamaguchi, M.; Kikushimia, K.; Hirao, T. An efficient vanadium-catalyzed bromination reaction. *Tetrahedron Lett*. **2007**, *48*, 2667.
11. Das, B.; Venkateswarlu, K.; Mahender, G.; Mahender, I. A simple and efficient method for α -bromination of carbonyl compounds using N-bromosuccinimide in the presence of silica-supported sodium hydrogen sulfate as a heterogeneous catalyst. *Tetrahedron Lett*. **2005**, *46*, 3041.
12. Das, B.; Ramu, R.; Ravikanth, B.; Reddy, K. R. Regioselective ring-opening of aziridines with potassium thiocyanate and thiols using sulfated zirconia as a heterogeneous recyclable catalyst. *Tetrahedron Lett.* **2006**, *47*, 779.
13. Das, B.; Venkateswarlu, K.; Krishnaiah, M.; Synthesis of β-chlorohydrins in water *Helv. Chim. Acta* 2007, *90*, 149.
14. Varvoglis, A. *Hypervalent Iodine in Organic Synythesis*; Academic: New York, 1997.
15. Wirth, T. Hypervalent iodine chemistry: Modern development in organic synthesis, In *Topics in Current Chemistry;* Springer: Berlin, 2003: p. 224.
16. Das, B.; Holla, H.; Mahender, G.; Banrjee, J.; Reddy, M. R. Hypervalent iodine-mediated interaction of aldoximes with activated alkenes including Baylis–Hillman adducts: A new and efficient method for the preparation of nitrile oxides from aldoximes. *Tetrahedron Lett*. **2004**, *45*, 7347.