An Efficient and Facile Hydroiodination of Alkenes and Alkynes Using Polymethylhydrosiloxane–Iodine System

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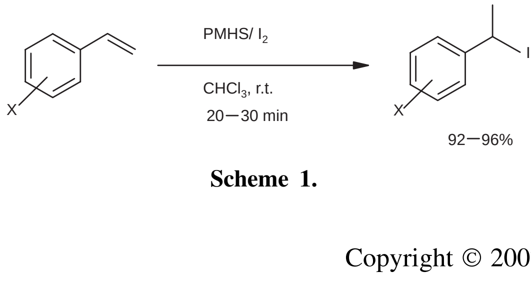
(Received March 19, 2007; CL-070290; E-mail: biswanathdas@yahoo.com)

A mild and efficient method has been developed for the synthesis of alkyl and alkenyl iodides from alkenes and alkynes using polymethylhydrosiloxane (PMHS) and iodine in chloroform at room temperature. The reagent system generates hydrogen iodide which regioselectively adds to the alkenes and alkynes.

Electrophilic addition of hydrogen halides to carbon–carbon double and triple bonds is one of the fundamental reactions in organic chemistry to synthesize alkyl and alkenyl iodides.[1] Alkyl iodides are widely utilized as starting material in organic synthesis.[1b] In general, the direct hydroiodination of olefins with hydriodic acid is the most suitable method for the preparation of alkyl iodides. Classically, this reaction is carried out with gaseous hydrogen iodide.[1] However, this method often leads to poor yields and side reactions because of uncontrollable iodine liberation. Moreover, HI is expensive to obtain commercially. As a result, several alternative methods have been reported for the synthesis of alkyl iodides, almost all generating hydriodic acid in situ using various reagents such as KI/orthophosphoric acid,[2a] iodine/alumina,[2b] borane-*N*,*N*-diethylaniline complex/I_2/acetic acid,[2c] chlorotrimethylsilane/NaI/water,[3a] iodotrimethylsilane alumina,[3b] aluminium triiodide/water,[3c] and CuO–HBF_4/I_2/Et_3SiH.[3d] Most of these methods suffer from various drawbacks such as need of excess reagents, high or low temperature, activation of catalyst, generation of complex reagent, longer reaction time, anhydrous condition, and incompatibility with other functional groups. The use of iodotrimethylsilane does not tolerate ester or acetal groups as well.[3b] Considering all the above laggings, there is still a need of clean and suitable methods for hydroiodination of olefins. In continuation of our work[4] in the catalytic application of molecular iodine, we have observed that the treatment of olefins with iodine and polymethylhydrosiloxane (PMHS) in chloroform at room temperature afforded the corresponding alkyl iodides in high yields, as depicted in Scheme 1.

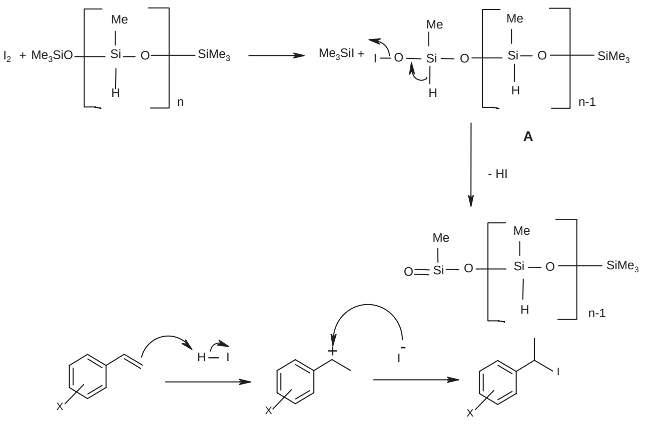


Scheme 1.

The reaction carried out with substituted alkenes afforded a single regioisomer, showing addition of hydrogen iodide following Markovnikov's[5] rule. However, methyl acrylate and acrylonitrile yielded methyl-3-iodopropanoate and 3-iodopropanenitrile (Table 1, Entries 10 and 11). The structures of the products were settled from their spectral (IR, ^{1}H NMR, and MS) and analytical data.[6]

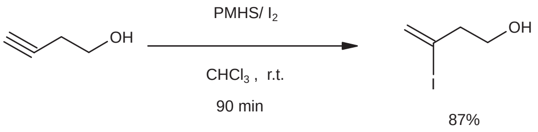
Utility of polymethylhydrosiloxane (PMHS), a co-product of the silicone industry, as an inert reducing agent for environmentally benign procedures is well documented.[7] However, to our knowledge, its use in combination with iodine for the synthesis of alkyl iodides has been explored here for the first time.

The probable mechanism is shown in Scheme 2. Iodine reacts initially with PMHS to produce trimethylsilyliodide and the unstable agent **A**.[7c] This in situ is forming hydriodic acid, which is taking part in the reaction.



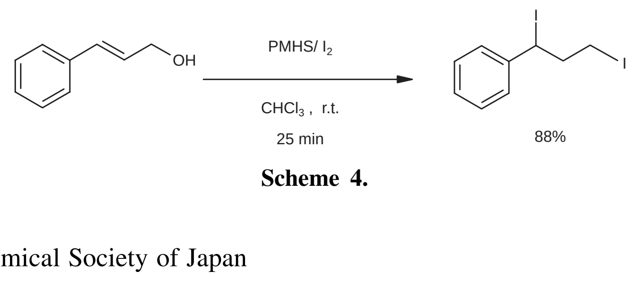
Scheme 2.

Further, the alkynes were also treated with PMHS/I_2 system to form the corresponding alkenyl iodides (Scheme 3). Reaction took comparatively longer duration (90 min) but again Markovnikov addition products were formed in high yields.



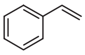
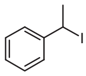
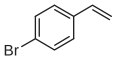
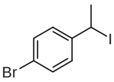
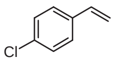
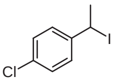
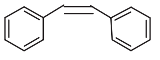
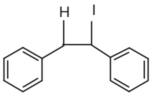
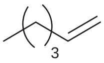
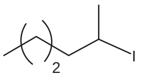
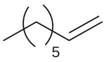
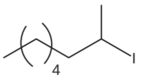
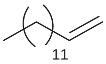
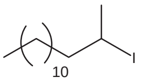
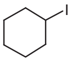
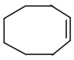
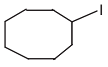
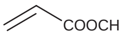
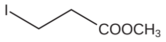
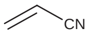
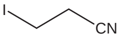
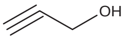
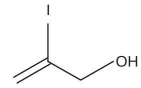
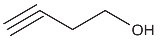
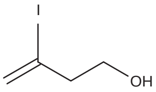
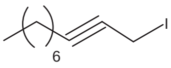
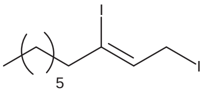
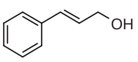
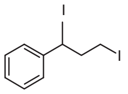
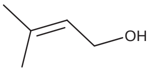
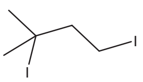
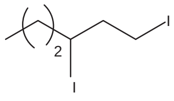
Scheme 3.

The regio- and stereochemistry of the vinyl iodide **2n** derived from the alkyne **1n** (Table 1) has been assigned on the basis of ^{1}H NMR spectral data.[8] Interestingly, in the case of cinnamyl alcohol, where an allylic alcohol system is present, the PMHS–I_2 system afforded 1,3-diiodopropyl benzene (Scheme 4), showing



Scheme 4.

Table 1. Preparation of alkyl and alkenyl iodides from alkenes and alkynes using PMHS/I_2[a]

Entry	Substrate **1**	Product **2**	Time /min	Isolated yield /%
1(a)			30	96
2(b)			30	92
3(c)			20	95
4(d)			30	90
5(e)			20	92
6(f)			20	94
7(g)			20	93
8(h)			25	88
9(i)			25	92
10(j)			30	94
11(k)			30	91
12(l)			90	84
13(m)			90	87
14(n)			90	86
15(o)			25	88
16(p)			25	90
17(q)			30	86

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

addition of hydrogen iodide to the C–C double bond as well as substitution of the allylic hydroxy by iodine.

This behavior of the reagent system was found to be consistent with other allylic alcohols such as 3-methylbut-2-en-1-ol (Entry 16) and (*E*)-hex-2-en-1-ol (Entry 17) leading to the formation of diiodo compounds.

In conclusion, PMHS–I_2 system is utilized here for the first time for hydroiodination of alkenes and alkynes under mild conditions. Operational simplicity, short reaction time, direct hydroiodination without side reactions, high yields, application of inexpensive chemicals, and impressive regioselectivity are the notable advantages of this method.

The authors thank CSIR and UGC, New Delhi for financial assistance.

References and Notes

\# Part 139 in the series "Studies on novel synthetic methodologies." IICT Communication No. 070519.

1 a) J. March, *Advanced Organic Chemistry*, 4th ed., Wiley, New York, **1985**. b) F. W. Stacey, J. F. Harris, *Org. React.* **1963**, *13*, 150.

2 a) H. Ston, H. Shechier, *Org. Synth.* **1963**, Coll. Vol. *4*, 543. b) R. M. Pagni, G. W. Kabalka, R. Boothe, K. Gaetano, L. J. Stewart, R. Conaway, C. Dial, D. Gray, S. Larson, T. Luidhart, *J. Org. Chem.* **1988**, *53*, 4477. c) C. K. Reddy, M. Periasamy, *Tetrahedron Lett.* **1990**, *31*, 1919.

3 a) S. Irifune, T. Kibayashi, Y. Ishii, M. Ogawa, *Synthesis* **1985**, 366. b) P. J. Kropp, K. A. Daus, M. T. Tubergen, K. D. Kepler, V. P. Wilson, S. L. Craig, M. M. Baillargeon, G. W. Breton, *J. Am. Chem. Soc.* **1993**, *115*, 3071. c) D. K. Dutta, K. C. Lekhok, R. C. Boruah, J. S. Sandhu, *Chem. Ind.* **1991**, 175. d) P. J. Campos, B. Garci, M. A. Rodriguez, *Tetrahedron Lett.* **2002**, *43*, 6111.

4 a) B. Das, K. R. Reddy, R. Ramu, P. Tirupathi, B. Ravikanth, *Synlett* **2006**, 1756. b) B. Das, B. Ravikanth, R. Ramu, K. Laxminarayana, B. Vittal Rao, *J. Mol. Catal. A: Chem.* **2006**, *255*, 74.

5 a) V. Markovnikoff, *Compt. Rend.* **1875**, *81*, 668.

6 Typical procedure for the preparation of alkyl iodides and alkenyl iodides: To a solution of styrene (0.5 mmol) or but-3-yn-1-ol (0.5 mmol) and PMHS (0.75 mmol) in chloroform (5 mL), iodine (0.5 mmol) was added. The reaction was allowed to stir at room temperature for 20–90 min and monitored by TLC. On completion, the solvent was evaporated under vacuum and the reaction mixture was dissolved in hexane and run through a silica-gel column using hexane–ethyl acetate system to afford the iodinated product in pure form. Spectral and analytical data of some alkyl iodides and alkenyl iodides are given below.
2b: IR (KBr): 3024, 2922, 1599, 1450, 962, 761, 691 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.40 (2H, d, $J = 8.0$ Hz), 7.26 (2H, d, $J = 8.0$ Hz), 5.26 (1H, q, $J = 7.0$ Hz), 2.18 (3H, d, $J = 7.0$ Hz); EIMS: m/z 183, 185 ($M^{+\bullet} - I$); Anal. Calcd for C_8H_8BrI: C, 30.87; H, 2.57%. Found: C, 30.78; H, 2.52%.
2d: IR (KBr): 2962, 1588, 1487, 1071, 1008, 819 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.40–6.92 (10H, m), 5.12 (1H, t, $J = 7.0$ Hz), 3.52 (1H, dd, $J = 13.5$, 7.0 Hz), 3.38 (1H, dd, $J = 13.5$, 7.0 Hz); EIMS: m/z 181 ($M^{+\bullet} - I$); Anal. Calcd for $C_{14}H_{13}I$: C, 54.55; H, 4.22%. Found: C, 54.47; H, 4.26%.
2m: IR (KBr): 3448, 2923, 2853, 1239, 1076, 1045, 798, 772 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz): δ 6.12 (1H, d, $J = 2.0$ Hz), 5.79 (1H, d, $J = 2.0$ Hz), 4.20 (2H, m), 2.88 (1H, m), 2.70 (1H, m); EIMS: m/z 71 ($M^{+\bullet} - I$); Anal. Calcd for C_4H_7IO: C, 24.24; H, 3.54%. Found: C, 24.28; H, 3.44%.
2o: IR (KBr): 2924, 2854, 1599, 1507, 1491, 1029, 755 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.42–7.20 (5H, m), 5.20 (1H, t, $J = 7.0$ Hz), 3.12 (2H, t, $J = 7.0$ Hz), 2.76 (1H, m), 2.45 (1H, m); EIMS: m/z 245 ($M^{+\bullet} - I$); Anal. Calcd for $C_9H_{10}I_2$: C, 29.03; H, 2.69%. Found: C, 29.11; H, 2.74%.

7 a) N. J. Lawrence, M. D. Drew, S. M. Bushell, *J. Chem. Soc., Perkin Trans. 1* **1999**, 3381. b) S. Chandrasekhar, G. Chandrasekhar, M. S. Reddy, P. Srihari, *Org. Biomol. Chem.* **2006**, *4*, 1650. c) J. S. Yadav, B. V. Subba Reddy, K. Premalatha, T. Swamy, *Tetrahedron Lett.* **2005**, *46*, 2687.

8 Supporting Information is available electronically on the CSJ-Journal Web site; http://www.csj.jp/journals/chem.-lett/index.htm.

Published on the web (Advance View) May 26, 2007; doi:10.1246/cl.2007.800