Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2013, 5(11):497-500

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Selective conversion of alcohols into the corresponding iodides with silica gel supported $I_2/HClO_4$ under microwave irradiation

M. Stalin Joseph*[1], Dilip C. Borah[2] and C. Isac Sobana Raj[3]

[1]*Department of Chemistry, Patkai Christian College (Autonomous), Nagaland, India*
[2]*D. C. B. Girls College, Jorhat, Assam, India*
[3]*Nesamony Memorial Christian College, Marthandam, Tamil Nadu, India*

ABSTRACT

A mild and efficient procedure for selective conversion of secondary, tertiary, benzylic and allylic alcohols into the corresponding iodides is described using silica gel supported iodine and perchloric acid under microwave irradiation.

Key words: Iodine, silica, Alcohol, Iodide. perchloric acid

INTRODUCTION

Alkyl iodides are important intermediates in organic synthesis [1]. These compounds are extensively used in different reactions like substitution, elimination, rearrangement and carbon-carbon coupling reactions. Alkyl and aryl iodides have a prominent role in the formation of carbon-carbon bonds through various reactions and are an important precursor for free radical generation and nucleophilic substitution [2]. Alkyl iodides finds an important role in organometallic chemisty in the synthesis of organometallic compounds. Since alkyl iodides are less stable than the corresponding chlorides and bromides so in turn it is found to be more active and even in some cases iodides are the only reactive halides [3, 4].

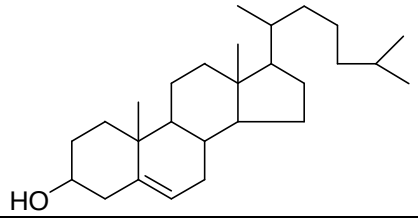
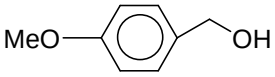
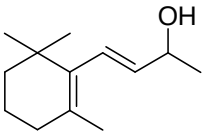
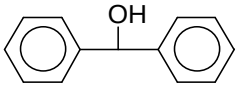
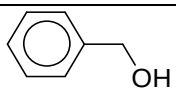
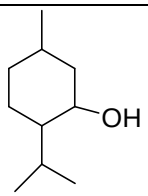
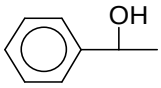
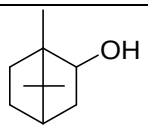
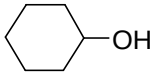
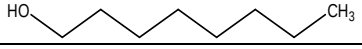
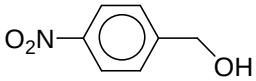
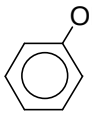
Alcohols are the most common precursors to the alkyl iodides. Various methods are available for the transformation of an alcohol to the corresponding iodide [5]. Few recent procedures for this transformation as reported in literature are KI/Silica-H_2SO_4 combination [6], CsI_2/TsOH combination [7], and $CeCl_3.7H_2O$/NaI over silica under microwave irradiation [8]. Solid supported reactions using silica gel, (both acidic and basic) clay and alumina under microwave irradiation becomes more attractive in modern synthesis. [9-12] The first method is selectively applicable to benzylic and allylic alcohols only while the next two are useful for primary, secondary, allylic as well as benzylic alcohols. Mention may be made of a few recent methods reported by different groups for the conversion of alcohol into iodide. Such methods are iodine in refluxing petroleum ether for secondary, tertiary and benzylic alcohols [13] KI/H_2SO_4 supported on natural kaolinitic clay under microwave irradiation [14], NaI over KSF-clay under microwave irradiation [15] and $CeCl_3.7H_2O$/NaI system [16] etc.

Although several methods are available for the conversion of alcohols into iodides yet a new, better and simpler methods using easy to use cheap chemicals are always welcome by synthetic chemists. During our endeavour to use iodine in various important reactions [17] it is observed that the silica supported iodine-perchloric acid combination is a very good reagent for conversion of alcohol into iodide under microwave irradiation. Herein we wish to report our method for this conversion.

EXPERIMENTAL SECTION

When a secondary alcohol like cholesterol is treated with iodine and perchloric acid under microwave irradiation for few minutes corresponding iodide is obtained in excellent yield. The reagent combination is selective and useful for secondary, tertiary, benzylic and allylic alcohols only. It has no effect on primary alcohols as well as on phenols. Ortho and para nitro-substituted benzyl alcohols are also found to be unreactive.

Table -1: Conversion of alcohols into corresponding iodides

S. No	Substrate	Yield (%) of the Iodide	Substrate recovered (%)	Reaction time (min)
1		97	-	2
2		95	-	4
3		87	7	2
4		73	15	5
5		56	35	6
6		72	20	5
7		65	35	3
8		60	30	8
9		53	40	5
10	$CH_3(CH_2)_{15}OH$	0	95	5
11		0	97	5
12		0	95	5
13		0	95	5

When the reaction was carried out in controlled experiment using iodine alone without perchloric acid under same reaction condition, the starting alcohol was recovered unchanged. This proves the utility of perchloric acid as a catalyst in the system. Separate experiments with iodine and concentrated nitric or sulfuric acid yielded mixture of

products with incomplete reaction. Another experiment with sodium iodide and perchloric acid under similar reaction conditions obviously resulted in good yield of the corresponding iodide. In case of the iodides obtained from optically pure menthol and borneol the $[\alpha]_D$ values were found to be –24.4 (c 1.8, $CHCl_3$) and –3.4 (c 0.34, $CHCl_3$) respectively as against the reported [9] values of –42.1 (c1.8, $CHCl_3$) and –8.8 (c 0.34, $CHCl_3$) indicating them to be racemic mixtures.

In a typical experiment, 100 mg of cholesterol (0.26 m mol) was dissolved in 5 ml of 1,2-dichloroethane in a 25 ml conical flask. To it 66 mg of Iodine-silica gel mixture (0.26 m mol) was added followed by one drop of $HClO_4$ (0.12 m mol). The purpose of silica gel is identified that it controls the vigorous reactive nature of $HClO_4$ during the addition of it. The mixture was subjected to microwave irradiation for 2 minutes at 360 watts in a microwave oven. The reaction mixture was cooled, filtered (in order to remove silica gel and can be recovered without much impurities) and diluted with chloroform. The organic layers was washed successively with a dilute solution of sodium thiosulphate and water and dried over anhydrous sodium sulphate. Removal of the solvent at reduced pressure yielded a mixture, which on purification by preparative TLC produced 127 mg (97%) of cholesteryl iodide. Thirteen different alcohols were taken as examples and the results are shown in the table below. All the products were characterized by comparison with authentic material as well as by spectroscopic methods [18].

RESULTS AND DISCUSSION

In contrast to the proposed SN^2 mechanism of iodide formation as suggested by Ravindranathan *et al* [13] the present reaction may be reasoned to proceed through SN^1 mechanism via formation of a carbocation. This carbocation is attacked by the available iodide ion giving rise to a product of racemic mixture. Reasoning for the proposed SN^1 mechanism is strengthened from the fact that the reaction is selective in the case of secondary, tertiary, benzylic and allylic alcohols only where formation of stabilized carbocation is easier. In case of primary alcohol and benzylic alcohol with electron withdrawing groups like $–NO_2$, the formation of a carbocation is not favourable and therefore the reaction does not take place in these substrates.
Not much literature is available on the reaction of iodine with perchloric acid. Formation of iodine perchlorate is reported [18] from the reaction of iodine, perchloric acid and ozone; but the product is low melting solid and readily hydrolysable material. In the present reaction, carbocation may be formed by the action of acid on the alcohol and it is attacked by the iodide ion formed from hydrolysis of iodine in the aqueous acid medium.

Acknowledgement
(This article is dedicated to our beloved mentor late. Dr. J. C. Sarma). Authors are grateful to the Director, NEIST, Jorhat for providing the facilities. DCB acknowledges the financial support from UGC, New Delhi in the form of Teacher Fellowship under FIP.

REFERENCES

[1] (a) R. Bohlmann In *Comprehensive Organic Synthesis*; B. M Trost, I Fleming, Eds.; Pergamon Press: Oxford, **1991**; Vol. 6, pp203. (b) R. D Chambers, S. R James, In *Comprehensive Organic Chemistry*; D Barton, W. D Ollis, Eds; Pergamon Press: Oxford, **1979**; Vol 1, pp493.
[2] B Giese, *Radicals in Organic Synthesis: Formation of carbon-carbon bonds*, Pergamon Press: Oxford, **1986**.
[3] J Yang, M Brookhart, *J. Am. Chem. Soc*. **2007**, *129*, 12656.
[4] J Villieras, C Bacquet, J. F Normant, *Bull. Chem. Soc. Fr*. **1975**, 1797.
[5] R.C Larock, *Comprehensive Organic Transformations: A guide to functional group preparations;* VCH Publishers, New York, **1989**, pp 358.
[6] A Hajipour, A Zarei, A Ruoho, *Synth. Commun*. **2006**, *36*, 1039.
[7] KM Khan, Zia-Ullah, S Perveen, G.M Maharvi, STA Shah, M Choudhury, Atta-ur-Rahman; W Voolter, *Letters in Org. Chem*. **2005**, *2*, 644.
[8] R Hosseinzadeh, M Tajbakhsh, Z Lasemi, A Sharifi, *Bull. Korean Chem. Soc*. **2004**, *25*, 1143.
[9] Fozia Ashrafa, Rajni Khajuriaband Khaliquz Zaman Khana *Journal of Chemical and Pharmaceutical Research*, **2013**, 5(8):33-36
[10]P..Lalitha, S Sivakamasundari, *J.Chem.Pharm.Res*, **2011, 2**(3),:387-393.
[11]Boudjemaa Boumoud*, Amel Zetchi, Taoues Boumoud and Abdelmadjid Debache. *Journal of Chemical and Pharmaceutical Research*, **2012**, 4(5):2517-2521
[12] Ashok D. Sagar,* Sadhana N. Chamle and Manjusha V. Yadav *Journal of Chemical and Pharmaceutical Research*, **2013**, 5(7):156-160
[13] R Joseph, P. S Pallan, A Sudalai, T Ravindranathan, *Tetrahedron Lett*. **1995**, *36*, 609.
[14] B. P Bandgar, V. S Sadavarte, S. V Bettigen, *Monatsh Chem.* **2002**, *133*, 345.
[15] G. L Kad, J Kaur, P Bansal, J Singh, *J. Chem. Research (S)*, **1996**, 188.

[16] M. D Deo, E Marcantoni, E Torregiani, G Bartoli, M. C Bellucci, M Bosco, L Sambri, *J. Org. Chem*. **2000**, *65*, 2830.
[17]a) I Saxena, D. C Borah, J. C Sarma, *Tetrahedron Lett.* **2005**, *46*, 1159. b) N Deka, J. C Sarma,. *Chemistry Lett.* **2001**, 794. c) N Deka, J. C Sarma, *J. Org. Chem.* **2001,** *66,* 1947. d) N Deka, J. C Sarma. *Synth. Commun.* **2000**, *30*, 4435. e) D. J Kalita, R Borah, J. C Sarma, *Tetrahedron Lett.* **1998**, *39*, 4573. f) N Deka, D. J Kalita, R Borah, J. C Sarma, *J. Org. Chem.* **1997,** *62*, 1563.
[18] J. E Macintyre, *Ed. Dictionary of Inorganic Compounds*, Chapman & Hall, **1992**, Vol.3, pp 2920.
[19]In spectral analysis the pertinent change observed between the spectra of substrate and product is the absence of OH absorption in IR spectrum of the product. In NMR spectrum the chemical shift of the proton on the iodine appeared little up field than the corresponding proton on the OH. Typical example: In case of cholesteryl iodide (entry 1) the NMR spectrum showed the broad multiplet of C-3 proton of cholesterol at 3.2 δ ppm to move up field to 3.0 ppm. In IR spectrum the absorption band due to OH group at 3400 cm^{-1} was absent in the iodide. Mass spectrum showed the M+ peak at m/z 496 followed by peaks at m/z 465, 339, 325, 311 etc. For p-methoxy benzyl iodide (entry 2) the absorption band due to OH group at 3400 cm^{-1} was absent in the IR spectrum of the iodide and in the NMR spectrum the singlet due to CH_2 protons is found to shift to 4.05 ppm from 4.15 ppm.