SYNLETT
Spotlight 352

This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

Sodium Iodide

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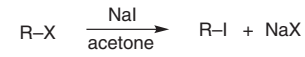
Introduction

Sodium iodide (NaI) occurs as colorless, odorless or as a white crystalline solid; it is slightly hygroscopic, and a commercially available reagent. It is soluble in water, alcohols, acetone, and other organic solvents and stable under normal temperature and pressure (mp: 651 °C, d = 3.67 g/cm^3).[1] On a laboratory scale, sodium iodide may be prepared by neutralizing a solution of sodium hydroxide or sodium carbonate with hydriodic acid.[2] Sodium iodide is a very useful and versatile reagent for the synthesis of various types of organic compounds. For example, an important application of this reagent involves the conversion of an alkyl chloride or alkyl bromide to an alkyl iodide by the addition of sodium iodide in acetone (Scheme 1).[3] This nucleophilic substitution reaction, also known as Finkelstein reaction, may proceed via either an S_N1 or S_N2 mechanism depending on the nature of the alkyl halide.[4,5]



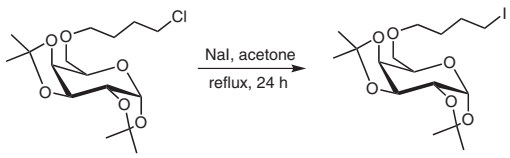
X = Cl or Br

Scheme 1

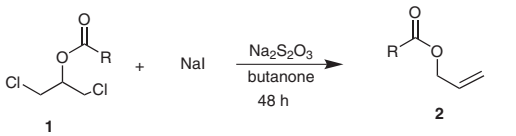
This reaction has been expanded to include the conversion of alcohols into alkyl halides by first converting the alcohol into a sulfonate ester (tosylates or mesylates are usually used), and then performing the substitution.[6] Other applications using sodium iodide as reagent in organic synthesis have been reported. They include the Finkelstein rearrangement–elimination reaction of 2-chloro-1-(chloromethyl)ethyl esters induced by NaI,[7] the Diels–Alder reaction between α,α,α′,α″-tetrabromo-oxylene and 2-cyclopentenone in the presence of NaI,[8] monoiodination of arenes by alkali metal iodide,[9] transformation of azides to primary amines using the $CeCl_3{\cdot}7H_2O$/NaI system,[11] and Michael addition of nucleophiles to alkenes promoted by the $CeCl_3{\cdot}7H_2O$/NaI system supported on alumina.[12]

Abstracts

(A) Möker and Thiem showed that the 4′-chloro substituent of the 6-*O*-(4′-chlorobutyl)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose was replaced by iodide in acetone under reflux for 24 h in a Finkelstein reaction to give the product 3-*O*-(4′-iodobutyl)-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose in 85% yield.[5]



(B) Eras et al. reported that 0.5 equivalent of sodium iodide (NaI) in butanone and the presence of a reducing agent like sodium thiosulfate induce the formation of the corresponding allyl esters **2**, starting from 2-chloro-1-(chloromethyl)ethyl alkyl or aryl esters **1** by the Finkelstein rearrangement–elimination reaction.[7]



1
R = $Me(CH_2)_{14}$
2-Naph

2
R = $Me(CH_2)_{14}$ 99%
2-Naph 94%

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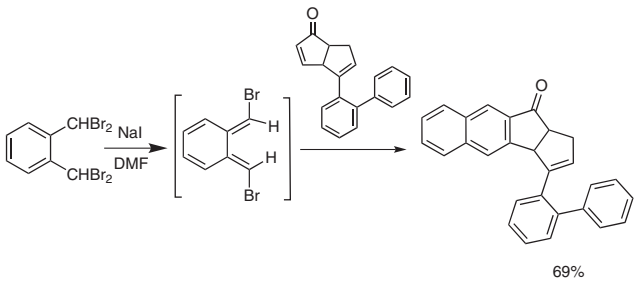
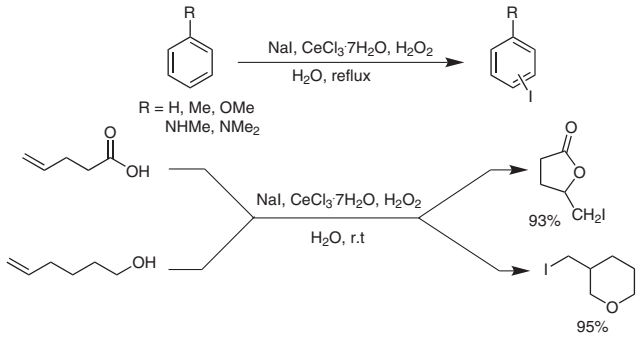
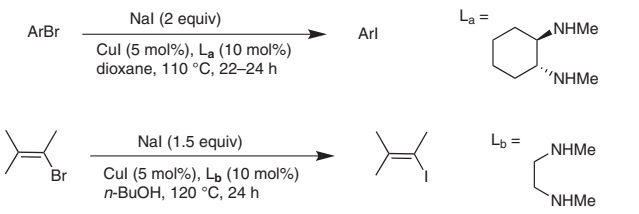
(C) Meyer and Hergenrother described the synthesis of 2,3-disubstituted naphthalene by Diels–Alder aromatization reaction between α,α,α′,α″-tetrabromo *o*-xylene and a 2-pentanone derivative in the presence of sodium iodide in DMF.[8]



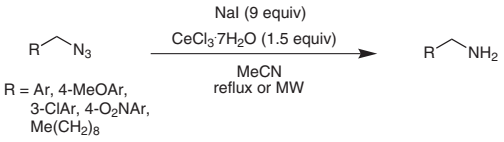
(D) Recently, Firouzabadi et al. reported a new environmentally friendly catalytic method for the efficient monoiodination of arenes. The method is based on using sodium iodide, hydrogen peroxide (35%) and cerium(III) chloride as an effective catalyst in water under reflux conditions. This method can also be applied easily in the syntheses of iodinated cyclic ethers and iodinated lactones from their corresponding unsaturated alcohols and carboxylic acids in high yield.[9]



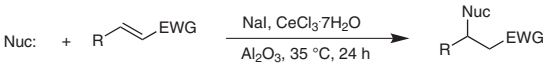
(E) A new method for the conversion of aryl, heteroaryl, and vinyl bromides into the corresponding iodides utilizing NaI, a catalyst system comprising CuI and a 1,2- or 1,3-diamine ligand was developed by Klapars and Buchwald. This method gives products in excellent yield.[10]



(F) Bartoli and co-workers described a simple and efficient method of converting azides into exclusively primary amines using NaI in the presence of inexpensive $CeCl_3 \cdot 7H_2O$ in refluxing acetonitrile or under microwave-assisted irradiation.[11]



(G) Bartoli and co-workers have also reported the hetero-Michel addition of nucleophilic nitrogen compounds to electron-poor alkenes promoted by the $CeCl_3 \cdot 7H_2O$/NaI system supported on alumina under solvent-free conditions.[12] The resulting β-amino derivatives are versatile synthons for the synthesis of many nitrogen-containing biologically important compounds.



References

(1) Kirk, R. E.; Othmer, D. F. *Encyclopedia of Chemical Technology*, 2nd ed., Vol. 18; John Wiley & Sons Ltd.: New York, **1969**, 485.
(2) Thorpe, J. F. *Thorpe's Dictionary of Applied Chemistry*, 4th ed., Vol. X; Longmans Green: London, **1950**, 871.
(3) Finkelstein, H. *Ber. Dtsch. Chem. Ges.* **1910**, *43*, 1528.
(4) Meloncelli, P. J.; Martin, A. D.; Lowary, T. L. *Carbohydr. Res.* **2009**, *344*, 1110.
(5) Möker, J.; Thiem, J. *Eur. J. Org. Chem.* **2009**, 4842.
(6) Šilhár, P.; Pohl, R.; Votruba, I.; Hocek, M. *Org. Biomol. Chem.* **2005**, *3*, 3001.
(7) Eras, J.; Escribà, M.; Villorbina, G.; Oromí-Farrús, M.; Balcells, M.; Canela, R. *Tetrahedron* **2009**, *65*, 4866.
(8) Meyer, S. T.; Hergenrother, P. J. *Org. Lett.* **2009**, *18*, 4052.
(9) Firouzabadi, H.; Iranpoor, N.; Kazemi, S.; Ghaderi, A.; Garzan, A. *Adv. Synth. Catal.* **2009**, *351*, 1925.
(10) Klapars, A.; Buchwald, S. L. *J. Am. Chem. Soc.* **2002**, *124*, 14844.
(11) Bartoli, G.; Di Antonio, G.; Giovannini, R.; Giuli, S.; Lanari, S.; Paoletti, M.; Marcantoni, E. *J. Org. Chem.* **2008**, *73*, 1919.
(12) Bartoli, G.; Bartolacci, M.; Giuliani, A.; Marcantoni, E.; Massaccesi, M.; Torregiani, E. *J. Org. Chem.* **2005**, *70*, 169.