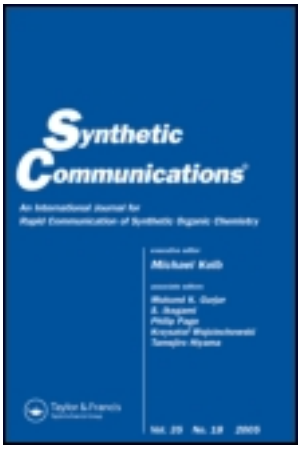

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Convenient and Efficient Method for the Iodination of Benzylic and Aliphatic Alcohols by Using $Al(HSO_4)_3$/KI in Nonaqueous Solution

Hassan Tajik [a] , Farhad Shirini [a] , Mohammad Ali Zolfigol [b] & Faeze Samimi [a]
[a] Department of Chemistry, Guilan University, Rasht, Guilan, Iran
[b] Department of Chemistry, Bu Ali Sina University, Hamadan, Iran
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Convenient and Efficient Method for the Iodination of Benzylic and Aliphatic Alcohols by Using $Al(HSO_4)_3$/KI in Nonaqueous Solution

Hassan Tajik and Farhad Shirini
Department of Chemistry, Guilan University, Guilan, Iran

Mohammad Ali Zolfigol
Department of Chemistry, Bu Ali Sina University, Hamadan, Iran

Faeze Samimi
Department of Chemistry, Guilan University, Guilan, Iran

Abstract: A simple and efficient method for the iodination of benzylic and aliphatic alcohols by using $Al(HSO_4)_3$/KI in *n*-hexane as solvent is reported. Mild reaction conditions and good to excellent yields of the products are the noteworthy advantages of the method.

Keywords: $Al(HSO_4)_3$, benzylic alcohols, benzylic iodides, iodination

Alkyl and aryl iodides are frequently used in organic chemistry for coupling reactions and organometallic synthesis. They can also be employed as intermediates in substitution and elimination reactions. Therefore, various methods have been reported for the synthesis of these compounds,[1–4] and benzylic and aliphatic iodides can be obtained from the corresponding

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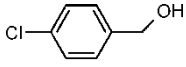
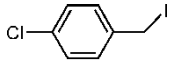
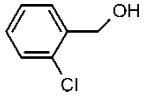
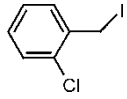
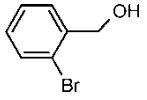
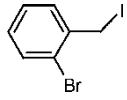
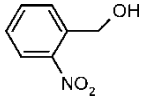
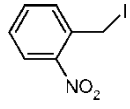
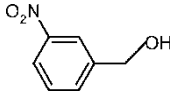
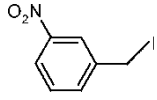
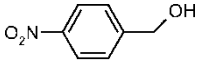
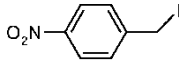
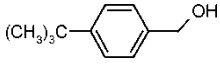
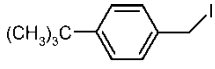
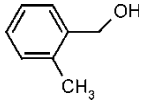
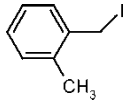
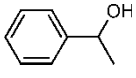
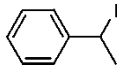
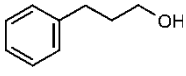
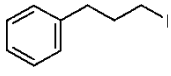
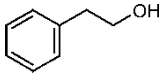
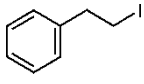
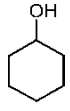
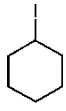
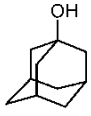
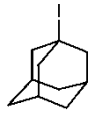
Address correspondence to Hassan Tajik, Department of Chemistry, Guilan University, Rasht, 41335-1914, Iran. E-mail: tajik@guilan.ac.ir and hasan_tajik@yahoo.com

Table 1. Iodination of some benzylic and aliphatic alcohols with $Al(HSO_4)_3/KI$[a] in *n*-hexane[b]

Entry	Substrate	Product(s)	Time (h)	Yield (%)[c]
1			0.5	90
2			0.5	95
3			0.5	95
4			2.0	90
5			3.0	92
6			2.0	85
7			0.5	96
8			1.0	93
9			0.5	93
10			1.0	87
11			0.5	85

(*continued*)

Table 1. Continued

Entry	Substrate	Product(s)	Time (h)	Yield (%)[c]
12			1.0	80
13			0.5	90

[a]Molar ratio of substrate/$Al(HSO_4)_3$/KI, 1 : 1 : 1.2.

[b]All of the reactions were performed at room temperature, except for the entries 4, 5, 6, and 10, which were performed under reflux conditions.

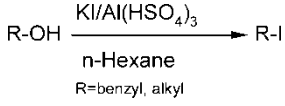
[c]Isolated yield.

alcohols by using a variety of systems such as $ClSiMe_3$/NaI,[5] $BF_3 \cdot Et_2O$/NaI,[6] $BF_3 \cdot Et_2O$/KI,[7] $CeCl_3 \cdot 7H_2O$/NaI,[8] Amberlist 15/NaI,[9] $(CH_3)_3SiI$,[10] and P_2I_4.[11]

Despite the variety of methods, some of them suffer from drawbacks such as contamination with side products, toxicity or low stability of the reagents, long reaction times, harsh reaction conditions, and low yields. To overcome some of the problems, new methods have been introduced in which low toxicity, greater stability of the reagents, mild reaction conditions, higher selectivity, and yields have been the focus of attention.[12,13]

We report herein a mild and efficient method for the iodination of benzylic and aliphatic alcohols by using potassium iodide as the iodine source and aluminium hydrogen sulfate[14,15] as the Lewis acid in *n*-hexane as solvent. The results are given in Table 1 (Scheme 1).

We first examined the reactions at room temperature and, when necessary, heated the mixture to reflux for the appropriate time. As shown in Table 1, this system is suitable for benzylic iodination of benzylic alcohols (Table 1, entries 1–9), and benzylic alcohols with electron-donating or electron-withdrawing groups on the rings were iodinated successfully. However, the rate of reaction was slower when the ring contains an electron-withdrawing group (Table 1, entries 4–8). The method can also be



Scheme 1.

employed for the conversion of aliphatic alcohols to the corresponding iodides in good yields (Table 1, entries 10–12). 1-Adamantanol, a tertiary alcohol, was converted to its iodide in good yield (Table 1, entry 13). The easy procedure, simple workup, short reaction times, and excellent to good yields of the products will make this method a useful addition to the available methodologies.

EXPERIMENTAL

All of the products were characterized by comparison of their physical and spectral data with those of the known samples or analyzing using GC or mass spectrometry. All chemicals were purchased from the Merck or Fluka Chemical Company. Aluminium hydrogen sulfate was prepared according to the previously reported method.[14,15]

Iodination of Alcohols with KI and $Al(HSO_4)_3$ in *n*-Hexane; General Procedure

$Al(HSO_4)_3$ (1 mmol) was added to a mixture of alcohol (1 mmol) and KI (1.2 mmol) in *n*-hexane (5 mL), and the resulting mixture was stirred at room temperature for 0.5–1.0 h or refluxed for 1–3 h. The progress of reaction was monitored by TLC (eluent: *n*-hexane/CCl_4, 1 : 2) or GC. After completion of the reaction, the mixture was filtered, and the filtrate was separated and diluted with *n*-hexane (5.0 mL). The resulting solution was transferred to a separatory funnel and washed with aqueous solution of $Na_2S_2O_3$ (0.1 M, 10 mL) and then H_2O (10 mL). The organic layer was separated and dried over anhydrous Na_2SO_4. Evaporation of the solvent under reduced pressure gave the pure product. If necessary, the product was purified by column chromatography (eluent: *n*-hexane/CCl_4, 1 : 2).

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