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An expedient and highly selective iodination of alcohols using a KI/BF_3·Et_2O system

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Abstract—Alkyl iodides are prepared in high yields by treatment of allylic and benzylic alcohols with an equimolar amount of KI in the presence of BF_3·Et_2O in dioxane under mild conditions. © 2001 Elsevier Science Ltd. All rights reserved.

Alkyl iodides or bromides are often used for ionic or radical carbon–carbon coupling reactions and can also act as intermediates in substitution reactions, elimination reactions and rearrangements. Therefore, the conversion of alcohols into alkyl halides is a very important transformation in organic chemistry. Although various methods have been reported in the literature[1–4] to achieve this goal, some of these require expensive reagents, long reaction times and tedious reaction work-up. Other methods involve mild conditions and the use of iodo[5] and bromotrimethylsilanes,[6] chlorotrimethylsilane–sodium iodide[7] and hexamethyldisilazane–iodine[8] as reagents. More recently, some useful reports[9–12] have been published regarding the selective conversion of allylic and benzylic and other (primary, secondary and tertiary) alcohols into halides. We found that the KI/BF_3·Et_2O system was effective for this transformation and this communication deals with the scope and limitations of this newly developed iodination method.

$$\underset{\mathbf{1}}{\textbf{R-OH}} \xrightarrow[\text{Dioxane, 25 °C}]{\text{KI/BF}_3\text{.Et}_2\text{O}} \underset{\mathbf{2}}{\textbf{R-I}}$$

R = allylic, benzylic

A variety of allylic and benzylic alcohols were converted into the corresponding iodides when treated with a molar equivalent of KI in the presence of BF_3·Et_2O. The reaction was found to proceed smoothly at room temperature within 5–30 min. Among various solvents studied, 1,4-dioxane was found to be the solvent of choice. The products were isolated by aqueous work-up followed by solvent extraction and were purified by column chromatography if necessary to afford pure alkyl iodide (Table 1).

The reaction was found to be highly selective as only allylic and benzylic alcohols are converted to iodides in high yields (84–95%), whereas saturated aliphatic alcohols did not yield iodides even after prolonged stirring in dioxane. The remarkable selectivity of this reaction allowed only allylic and benzylic hydroxyls to be iodinated without affecting other OH groups present in the molecule (entries 6, 12). Furthermore, a secondary OH group at an allylic or benzylic position could easily be substituted by an iodide group in high yields using this technique. As the reaction proceeds with gradual consumption of BF_3·Et_2O by the byproduct KOH, a molar equivalent of BF_3·Et_2O is essential in order to achieve complete conversion of the alcohol.

In conclusion, the highly selective, simple, mild, direct and high yielding iodination of allylic and benzylic alcohols using KI/BF_3·Et_2O system in dioxane, presented in this paper, serves as a useful synthetic entry to valuable alkyl iodides.

Conversion of benzylic and allylic alcohols into iodides—general procedure: The alcohol (5 mmol) was dissolved in dry 1,4-dioxane (10 ml) to which BF_3·Et_2O (5 mmol) and KI (5 mmol) were added and the resulting mixture was stirred at room temperature. After the complete conversion of alcohol to iodide (TLC) the reaction mixture was poured into cold water and extracted with

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Keywords: alcohols; iodides; BF_3·Et_2O; selective iodination.

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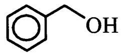
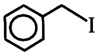
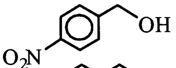
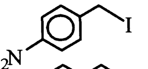
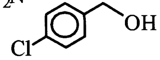
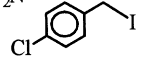
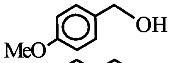
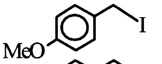
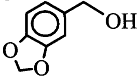
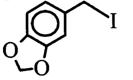
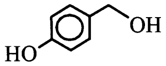
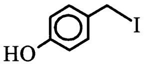
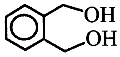
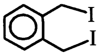
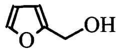
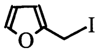
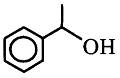
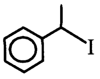
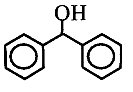
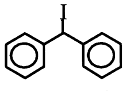
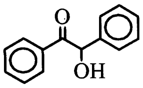
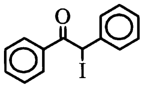
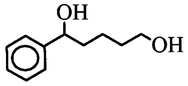
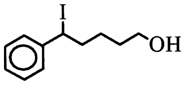
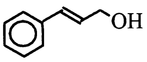
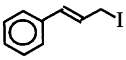
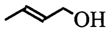
Table 1. Conversion of alcohols to iodides using a KI/$BF_3 \cdot Et_2O$ system at 25°C

Entry	Substrate	Product	Time (min.)	Yield^{a,b} (%)
1	 **(1a)**	 **(2a)**	5	95
2	 **(1b)**	 **(2b)**	30	91
3	 **(1c)**	 **(2c)**	15	93
4	 **(1d)**	 **(2d)**	30	90
5	 **(1e)**	 **(2e)**	30	84
6	 **(1f)**	 **(2f)**	20	91
7	 **(1g)**	 **(2g)**	25	95
8	 **(1h)**	 **(2h)**	10	91
9	 **(1i)**	 **(2i)**	15	95
10	 **(1j)**	 **(2j)**	15	94
11	 **(1k)**	 **(2k)**	15	85
12	 **(1l)**	 **(2l)**	20	85
13	 **(1m)**	 **(2m)**	20	85
14	 **(1n)**	 **(2n)**	15	85
15	*n*-Octanol **(1o)**	No Reaction	60	—
16	Isoamyl alcohol **(1p)**	No Reaction	60	—
17	Cyclohexanol **(1q)**	No Reaction	60	—
18	*t*-Butyl alcohol **(1r)**	No Reaction	60	—

[a] Yields of isolated products.

[b] Products are characterised by spectral and elemental analysis.[13]

diethyl ether (3×10 ml). The combined organic layer was washed with water and brine, dried (Na_2SO_4) and the solvent was evaporated under reduced pressure. The product was purified wherever necessary by column chromatography on silica gel using hexane/ethyl acetate (9:1) as an eluent to afford pure alkyl iodide.

Acknowledgements

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13. Compound **2c**: IR (Neat, cm^{-1}): 644, 711, 805, 831, 1013, 1086, 1153, 1177, 1212, 1407, 1422, 1488, 1503, 1592, 1901, 2910, 3010. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 4.41$ (s, 2H, $ArCH_2$), 7.29 (m, 4H, Ar-H). Anal. calcd for C_7H_6ClI (252.4342): C, 33.81; H, 2.38; Cl, 14.05; I, 50.27. Found: C, 33.78; H, 2.42; Cl, 13.98; I, 50.33.

    Compound **2d**: IR (Neat, cm^{-1}): 695, 810, 835, 1090, 1260, 1470, 1605, 2910. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.77$ (s, 3H, OCH_3), 3.86 (s, 2H, $ArCH_2$), 6.82 (d, 2H, Ar-H), 7.07 (d, 2H, Ar-H). Anal. calcd for C_8H_9OI (247.9919); C, 38.75; H, 3.63; I, 51.17. Found: C, 38.79; H, 3.59; I, 51.21.

    Compound **2e**: IR (KBr, cm^{-1}): 630, 650, 710, 841, 934, 1039, 1117, 1258, 1218, 1483, 1503, 1620, 2895, 3010, 3120. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.81$ (s, 2H, $ArCH_2$), 4.7 (s, 2H, O-CH_2-O), 7.02 (m, 3H, Ar-H). Anal. calcd for $C_8H_7O_2I$ (254.9913): C, 37.68; H, 2.75; I, 49.77. Found: C, 37.72; H, 2.78; I, 49.84.

    Compound **2f**: IR (KBr, cm^{-1}): 696, 1091, 1260, 1475, 1608, 2850, 2919, 3450 (br). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.69$ (s, 2H, $ArCH_2$), 6.74 (d, 2H, Ar-H), 6.91 (d, 2H, Ar-H). Anal. calcd for C_7H_7OI (233.9809): C, 35.93; H, 2.99; I, 54.23. Found: C, 35.88; H, 3.01; I, 54.26.

    Compound **2h**: IR (Neat, cm^{-1}): 699, 801, 1023, 1097, 1261, 1463, 1603, 2852, 2923, 2961. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.75$ (s, 2H, $ArCH_2$), 7.04 (s, 3H, Ar-H). Anal. calcd for C_5H_5OI (207.9589): C, 28.88; H, 2.40; I, 61.02. Found: C, 28.85; H, 2.42; I, 60.97.

    Compound **2i**: IR (KBr, cm^{-1}): 699, 761, 850, 960, 1020, 1210, 1300, 1451, 1493, 1602, 2730, 2850, 2963, 3010, 3120. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.68$ (d, 3H, CH_3), 4.8 (q, 1H, Ar-CH), 7.1 (s, 5H, Ar-H). Anal. calcd for C_8H_9I (232.0874): C, 41.40; H, 3.88; I, 54.68. Found: C, 41.44; H, 3.85; I, 54.73.

    Compound **2j**: IR (KBr, cm^{-1}): 638, 699, 734, 919, 1027, 1058, 1185, 1236, 1278, 1318, 1449, 1493, 1598, 1660, 2810, 2910, 3026, 3061. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 4.6$ (s, 1H, Ar-CH), 7.15 (s, 10H, Ar-H). Anal. calcd for $C_{13}H_{11}I$ (294. 1424): C, 53.08; H, 3.74; I, 43.18. Found: C, 53.11; H, 3.77; I, 43.21.

    Compound **2k**: IR (KBr, cm^{-1}): 635, 697, 810, 935, 1020, 1058, 1503, 1607, 1720, 2827, 2921, 3026. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 4.9$ (s, 1H, Ar-CH), 7.11 (s, 5H, Ar-H), 7.2 (s, 5H, Ar-H). Anal. calcd for $C_{14}H_{11}OI$ (323.0579): C, 52.05; H, 3.40; I, 39.59. Found: C, 52.11; H, 3.38; I, 39.64.

    Compound **2m**: IR (KBr, cm^{-1}): 699, 755, 1031, 1130, 1451, 1499, 1598, 1653, 2851, 2827, 2921, 3033. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.4$ (d, 2H, CH_2I), 6.6 (m, 1H, =CH), 6.8 (d, 1H, ArCH), 7.20 (s, 5H, Ar-H). Anal. calcd for: C_9H_9I (245.0035): C, 44.13; H, 3.67; I, 52.21. Found: C, 44.09; H, 3.65; I, 52.14.