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A Convenient Method for the Preparation of Highly Pure *t*-Alkyl Bromides and Iodides

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Synopsis. Highly pure (99—100%) *t*-butyl and *t*-pentyl bromides and iodides, and 3-bromo-3-ethylpentane were readily prepared in 83—95% yields by the reactions of the corresponding alcohols with hydrobromic or hydroiodic acid, using lithium or calcium halide. The metal halides remarkably increased the yield and the purity of the products.

t-Alkyl bromides have been commonly prepared by the addition of hydrogen bromide to olefins[1] and by the reactions of *t*-alkyl alcohols with phosphorus(III) bromide,[2] hydrobromic acid,[3,4] or bromine and triphenylphosphine.[5] *t*-Alkyl iodides have been prepared by the reactions of the corresponding alcohols with potassium iodide and phosphoric acid,[6] or with trimethylsilyl iodide,[7] and by the iodination of *t*-alkyl chlorides.[8] However, the above preparations are not always satisfactory with regard to the purity and the yield of the product and the reaction conditions. The commercially available *t*-butyl bromide and iodide are contaminated by impurities (4—5%) which can not be readily removed.

We wish now to report a convenient and selective method of preparing highly pure *t*-alkyl bromides and iodides under very mild conditions, using lithium and calcium halides.

Results and Discussion

Table 1 shows the brominations of *t*-alkyl alcohols. The reactions of *t*-butyl alcohol with two and five molar equivalents of hydrobromic acid were carried out in the absence of the metal bromides at 0 °C to give *t*-butyl bromide in yields of only 9 and 43% respectively. By contrast, the yield of the bromide was increased up to 85% in the reaction of *t*-butyl alcohol with hydrobromic acid and metal bromide (molar ratio 1:2:1.5). A further excess of hydrobromic acid or metal bromide did not, though, improve the yield significantly. The product after simply being washed with ethylene glycol was 99.7—99.8% pure, with the only impurity being 0.2—0.3% of 2-methylpropene. Sodium and magnesium bromides were not effective for use in the preparation because of their poor solubility in hydrobromic acid. Similar brominations of *t*-pentyl alcohol and 3-ethyl-3-pentanol using metal bromides were also carried out to give the corresponding bromides of a high purity in 91 and 93% yields respectively.

Table 2 shows the iodinations of *t*-alkyl alcohols. The iodinations of *t*-butyl and *t*-pentyl alcohols with two equivalents of hydroiodic acid gave the corresponding iodides in only 21 and 35% yields respectively. The addition of 1—1.5 molar equivalents of lithium or calcium iodide to the system afforded highly pure *t*-butyl and *t*-pentyl iodides in 80—84% yields. Furthermore, the pure iodides could be readily obtained by the vacuum distillation of these highly pure products at room temperature.

On the whole, the metal halides in the reaction system remarkably increased the yield and the purity of the product. The hindered *t*-pentyl halides and 3-bromo-3-ethylpentane were more readily prepared than *t*-butyl halides. The hydrolysis of *t*-alkyl halides was much retarded by the addition of metal halides. Therefore, the halogenation of *t*-alkyl alcohols is in equilibrium with the hydrolysis, and the equilibrium is shifted very far to the right by these metal halides:

$$t\text{-ROH} + \text{HX(aq)} \overset{\text{MX}_n}{\rightleftarrows} t\text{-RX} + \text{H}_2\text{O}$$

TABLE 1. BROMINATIONS OF *t*-ALKYL ALCOHOLS WITH HYDROBROMIC ACID AND METAL BROMIDES

Alcohol[a]	HBr mol	Additive (mol)	Temp/°C	Time/h	Yield/% of product[b]	Purity/% of product GLPC	Titrn.[c]
t-BuOH	0.2	None	0	4	9	99.3	99.4
t-BuOH	0.5	None	0	2	43	99.6	—
t-BuOH	0.2	LiBr (0.1)	0	2	77	99.6	99.7
t-BuOH	0.2	LiBr (0.15)	0	2	85	99.8	99.7
t-BuOH	0.2	LiBr (0.2)	0	2	87	99.8	99.8
t-BuOH	0.3	LiBr (0.15)	0	2	84	99.7	99.6
t-BuOH	0.3	$CaBr_2$ (0.15)	0	2	85	99.7	99.8
t-$C_5H_{11}OH$	0.2	None	−10	2	33	93.6	—
t-$C_5H_{11}OH$	0.2	LiBr (0.15)	−10	2	91	99.3	99.2
t-$C_5H_{11}OH$	0.3	$CaBr_2$ (0.15)	−10	2	86	98.9	98.8
Et_3COH	0.2	None	−15	3	51	85.4	—
Et_3COH	0.2	LiBr (0.15)	−15	3	93	99.2	99.6
Et_3COH	0.2	LiBr (0.2)	−15	3	95	99.2	99.6

a) A 0.1-mol quantity of *t*-alkyl alcohol was used. b) Isolated yield of *t*-alkyl bromide based on *t*-alkyl alcohol. c) Determined by titration with 0.1 M aqueous sodium hydroxide.

TABLE 2. IODINATIONS OF *t*-ALKYL ALCOHOLS WITH HYDROIODIC ACID AND METAL IODIDES

Alcohol[a)]	HI mol	Additive (mol)	Temp °C	Time h	Yield/% of product[b)]	Purity/% of product GLPC	Titrn.[c)]
t-BuOH	0.2	None	0	1.5	21	99.2	—
t-BuOH	0.1	LiI (0.1)	0	1.5	74	99.7	99.7
t-BuOH	0.2	LiI (0.1)	0	1	80	99.7	99.7
t-BuOH	0.2	LiI (0.15)	0	0.5	83	99.8	99.8
t-BuOH	0.2	CaI_2 (0.1)	0	1	82	99.8	99.8
t-$C_5H_{11}OH$	0.2	None	−10	2	35	92.8	—
t-$C_5H_{11}OH$	0.2	LiI (0.15)	−10	2	84	99.1	99.4
t-$C_5H_{11}OH$	0.2	CaI_2 (0.1)	−10	2	82	99.1	99.4

a) A 0.1-mol quantity of *t*-alkyl alcohol was used. b) Isolated yield of *t*-alkyl iodide based on *t*-alkyl alcohol. c) Determined by titration with 0.1 M aqueous sodium hydroxide.

Experimental

The purity of the *t*-alkyl bromides and iodides was confirmed by GLPC and by titration with 0.1 M aqueous sodium hydroxide.[9)] GLPC analyses were performed on a 3 m×3 mm column packed with 5% Silicone DC 550 or 5% Didecyl phthalate, at 50—60 °C and at the carrier gas (helium) flow rate of 60—80 cm³/min. NMR spectra were recorded on a Hitachi NMR R-24B spectrometer operating at 60 MHz. Chemical shifts are reported in δ units, with tetramethylsilane as an internal standard.

Materials and Preparation. Lithium and calcium halides were of a commercial grade and were used without further purification. Hydrobromic acid (47%) and hydroiodic acid (55%) were GR grade reagents obtained from Nakarai Chemicals Co. *t*-Butyl and *t*-pentyl alcohols were distilled from sodium. 3-Ethyl-3-pentanol was prepared from diethyl ketone and ethylmagnesium bromide.

t-Butyl Bromide: Hydrobromic acid (23.2 cm³, 0.2 mol) was added, drop by drop, to a mixture of lithium bromide (13.03 g, 0.15 mol) and *t*-butyl alcohol (7.412 g, 0.1 mol) at 0 °C in a 100-cm³ Erlenmeyer flask. The mixture was then stirred magnetically for 2 h. The upper organic layer was separated and washed with ethylene glycol (10 cm³×3) to remove the hydrobromic acid and the remaining *t*-butyl alcohol, and was then dried over anhydrous sodium sulfate, giving 11.72 g (85%) of 99.8% pure *t*-butyl bromide; this was later distilled *in vacuo* to give the pure bromide as a colorless liquid: bp 73.1 °C; NMR ($CDCl_3$) δ=1.78 (9H, s, *t*-Bu).

t-Pentyl Bromide: Yield, 91%; bp 107.4 °C; NMR ($CDCl_3$) δ=1.09 (3H, t, J=7.2 Hz, CH_2CH_3), 1.78 (6H, s, *gem*-CH_3), and 1.82 (2H, q, J=7.2 Hz, CH_2).

3-Bromo-3-ethylpentane: Yield, 93%; bp 55 °C/15 Torr;† NMR ($CDCl_3$) δ=0.99 (9H, t, J=7.2 Hz, CH_3) and 1.90 (6H, q, J=7.2 Hz, CH_2).

t-Butyl Iodide: Yield, 83%; bp 26 °C/50 Torr; NMR ($CDCl_3$) δ=1.95 (9H, s, *t*-Bu).

t-Pentyl Iodide: Yield, 84% bp 25 °C/15 Torr; NMR ($CDCl_3$) δ=1.06 (3H, t, J=6 Hz, CH_2CH_3), 1.66 (2H, q, J=7 Hz, CH_2), and 1.91 (6H, s, *gem*-CH_3).

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† 1 Torr=(101325/760) Pa.