Oxidation Using Quaternary Ammonium Polyhalides. V.[1] Selective Oxidation of Benzyl Alcohols by the Use of Benzyltrimethylammonium Tribromide

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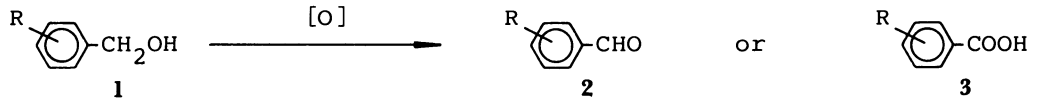
Synopsis. The reaction of several substituted benzyl alcohols with 1 equiv of benzyltrimethylammonium tribromide (BTMA Br_3) in carbon tetrachloride under basic or neutral conditions gave the corresponding benzaldehydes, and with 2 equiv of BTMA Br_3 in aqueous alkaline solution and subsequent acid hydrolysis gave the corresponding benzoic acids, respectively, in satisfactory yields.

Benzyltrimethylammonium tribromide (BTMA Br_3) has recently been introduced as a useful brominating agent by us.[2] During the course of our further investigation on the synthetic utility of BTMA Br_3, we have found that this reagent is also an effective oxidizing agent.[3] In this paper we wish to report on the selective oxidation of several benzyl alcohols **1** to the corresponding benzaldehydes **2** or benzoic acids **3** by the use of BTMA Br_3.

Results and Discussion

Although a variety of substituted **1** has been

Table 1. Oxidation of Benzyl Alcohols **1** to Benzaldehydes **2** and Benzoic Acids **3** with BTMA Br_3



1 **2** **3**

1	R	Molar ratio		Reaction conditions		Product		Isolated yield
		BTMA Br_3/1	NaOH/1	Temp/°C	Time/h	2	3	
1a	H	1	—[a]	70	24	**2a**	—	83
		2	8	rt	6	—	**3a**	98
1b	2-Me	1	3	rt	24	**2b**	—	50[b]
		2	8	rt	22	—	**3b**	90
1c	4-Me	1	3	rt	24	**2c**	—	**53**[b]
		2	8	rt	6	—	**3c**	96
1d	4-isoPr	1	3	rt	24	**2d**	—	—[c]
		2	8	rt	24	—	**3d**	50
1e	4-OMe	1	3	rt	15	**2e**	—	75
		2	8	rt	6	—	**3e**	96
1f	2,5-di-OMe	1	3	rt	24	**2f**	—	58[b]
		2	8	rt	20	—	**3f**	69
1g	3,4-di-OMe	1	3	rt	24	**2g**	—	84
		2	8	rt	17	—	**3g**	77
1h	3,4-OCH_2O-	1	3	rt	17	**2h**	—	76
		2	8	rt	20	—	**3h**	99
1i	2-Cl	1	—[d]	rt	3	**2i**	—	51[e]
		2	8	rt	20	—	**3i**	87
1j	3-Cl	1	—[d]	70	22	**2j**	—	60
		2	8	70	17	—	**3j**	94
1k	4-Cl	1	—[a]	rt	24	**2k**	—	54[e]
		2	8	rt	6	—	**3k**	94
1l	4-Br	1	—[d]	70	22	**2l**	—	63
		2	8	rt	8	—	**3l**	95
1m	2-NO_2	1	—[d]	70	33	**2m**	—	31[e]
		2	8	rt	19	—	**3m**	99
1n	3-NO_2	1	—[a]	70	34	**2n**	—	97
		2	8	rt	19	—	**3n**	94
1o	4-NO_2	1	—[a]	70	27	**2o**	—	87
		2	8	70	15	—	**3o**	98

a) The reaction was done in water without using alkali. b) The desired **2** was separated from the starting material by column chromatography on alumina, and a small amount of the corresponding sodium benzoate was found in the resulting alkaline solutions as by-product. c) A mixtures of **1d** and **2d**, which was not separated by column chromatography on alumina, was obtained. d) The reaction was done in aq Na_2HPO_4 solution (molar ratio: Na_2HPO_4/**1**=2). e) Considerable amount of the starting material was recovered because of its relatively poor reactivity.

converted into the corresponding **2** by means of a number of oxidizing agents,[4] we have found that BTMA Br_3 is also a convenient reagent to oxidize **1** into **2**. That is, the reaction of **1** with 1-equiv of BTMA Br_3 in carbon tetrachloride in the presence of an aqueous alkaline solution, an aqueous solution of Na_2HPO_4, or water, at room temperature or at 70 °C gave **2** in satisfactory yields. The results are summarized in Table 1.

It should also be mentioned that primary alcohols can be oxidized to carboxylic acids by many strong oxidizing agent including chromic acid, permanganate, and nitric acid. However, a few oxidizing agents[5] have been used for the direct conversion of **1** to **3**. We have also found that BTMA Br_3 can be used as a reagent for the oxidation of **1** to **3**. That is, the reaction of **1** with 2-equiv of BTMA Br_3 in an aqueous alkaline solution at room temperature or at 70 °C afforded **3** in good yields. The results are summarized in Table 1.

These reactions, which occurred under basic conditions, can be represented by the following equations:

$$\underset{\mathbf{1}}{\text{Ar-CH}_2\text{OH}} + \text{BTMA Br}_3 + 2\text{NaOH} \longrightarrow \underset{\mathbf{2}}{\text{Ar-CHO}} + \text{BTMA Br} + 2\text{NaBr} + 2\text{H}_2\text{O} \quad (1)$$

$$\mathbf{1} + 2\text{BTMA Br}_3 + 5\text{NaOH} \longrightarrow \text{Ar-COONa} + 2\text{BTMA Br} + 4\text{NaBr} + 4\text{H}_2\text{O} \xrightarrow{\text{H}_3\text{O}^+} \underset{\mathbf{3}}{\text{Ar-COOH}} \quad (2)$$

We assumed that the active species for the oxidation is sodium hypobromite or hypobromous acid, which may be produced from the reaction of BTMA Br_3 with aqueous sodium hydroxide or water, respectively.

As shown in Eqs. 1 and 2, oxidation products **2** or **3** can be obtained selectively from **1** by the use of a stoichiometric amount of BTMA Br_3. However, in these oxidation reactions of **1** (particulary active **1** such as methoxy-substituted benzyl alcohols (e.q., **1e**, **1f**, and **1g**)), an excess amount of alkali was required in order to avoid any aromatic bromination of **1**. Furthermore, the oxidation of **1** (which substituted an electron-attracting group) to **2** required more severe reaction conditions.

We emphasize that the above-mentioned procedure for the oxidation of **1** affording **2** or **3** should be a useful method owing to its simplicity, good yield of the product, and excellent selectivity.

Experimental

All products were characterized by comparing their ^1H NMR spectra and mp or bp with those of authentic samples or reported data.

Oxidation of 4-Methoxybenzyl Alcohol (1e) to 4-Methoxybenzaldehyde (2e); Typical Procedure: A solution of BTMA Br_3 (2.05 g, 5.25 mmol) and sodium hydroxide (0.60 g, 15 mmol) in water (25 ml) was added dropwise into a solution of **1e** (0.69 g, 5 mmol) in carbon tetrachloride (25 ml). The mixture was stirred at room temperature for 15 h until the initial yellow color faded. To the mixture was added 5% aq solution of $NaHSO_3$ (5 ml). Then, the carbon tetrachloride layer was separated and the water layer extracted with dichloromethane (30 ml×3). The organic layer was dried over $MgSO_4$, filtered, and evaporated under reduced pressure to give **2e** as a colorless liquid; yield 0.51 g (75%); bp 243—244 °C/760 mmHg (lit,[6] bp 248 °C/760 mmHg; 1 mmHg≈133.322 Pa).

Oxidation of 3-Chlorobenzyl Alcohol (1j) to 3-Chlorobenzoic Acid (3j); Typical Procedure: Compound **1j** (0.71 g, 5 mmol) was added into a solution of BTMA Br_3 (4.09 g, 10.5 mmol) and sodium hydroxide (1.60 g, 40 mmol) in water (30 ml). The mixture was stirred at 70 °C for 17 h until the initial yellow color faded. To the mixture was added a 5% aq solution of $NaHSO_3$ (5 ml); the mixture was then acidified sufficiently with 6M-HCl. The solution was extracted with ether (40 ml×4) and the ether layer was dried over $MgSO_4$, filtered, and evaporated under reduced pressure to give **3j** as a colorless crystals; yield 0.73 g (94%); mp 156—157 °C (lit,[7] mp 156—157 °C).

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