

# Bromination of Phenols by Use of Benzyltrimethylammonium Chlorobromate(1-)<sup>1)</sup>

Shoji KAJIGAESHI\*, Takaaki KAKINAMI\*\*, Masayuki MORIWAKI\*\*\*,  
Shizuo FUJISAKI\*, and Tsuyoshi OKAMOTO\*\*

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## Abstract

The reaction of phenols with benzyltrimethylammonium chlorobromate(1-) in dichloromethane-methanol for several minutes at room temperature gave easily polybromophenols in quantitative yields.

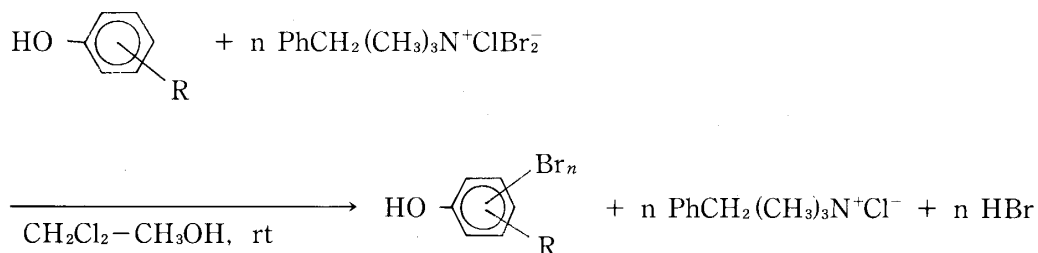
## Introduction

It has previously been shown in our laboratories that the reaction of phenols(I) with tetraalkylammonium tribromide such as benzyltrimethylammonium tribromide (BTMA Br<sub>3</sub>)<sup>2,3)</sup> and tetrabutylammonium tribromide (TBA Br<sub>3</sub>)<sup>3)</sup> in dichloromethane-methanol at room temperature gave bromophenols(II) in good yields, respectively. Furthermore, we wish to report the bromination of I by use of a new reagent benzyltrimethylammonium chlorobromate(1-) (BTMA ClBr<sub>2</sub>).

## Results and Discussion

Reaction of benzyltrimethylammonium chloride with equimolar amount of bromine in dichloromethane gave BTMA ClBr<sub>2</sub> (stable orange crystals, mp 101-102°C) in good yield.

Reaction of I with BTMA ClBr<sub>2</sub> in dichloromethane-methanol for several minutes at room temperature readily gave II in quantitative yields. The results are summarized in Table 1.




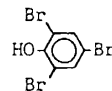

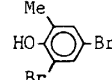

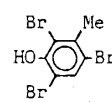
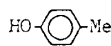
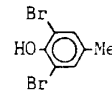
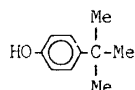
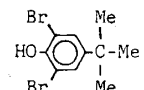

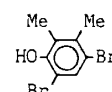

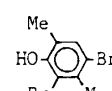

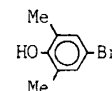
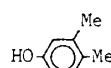
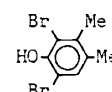

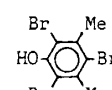

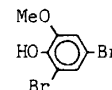
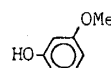
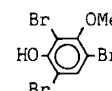

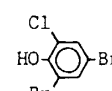

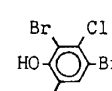
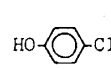
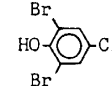
It has been found that brominating intensities of the three reagents (TBA Br<sub>3</sub>, BTMA Br<sub>3</sub>, and BTMA ClBr<sub>2</sub>) for I follow in the next order; BTMA ClBr<sub>2</sub> >> BTMA Br<sub>3</sub> > TBA Br<sub>3</sub>. For instance, 2, 4, 6-tribromophenol(II-1) has been obtained from

\*Department of Industrial Chemistry

\*\*Department of Industrial Chemistry, Ube Technical College

\*\*\*Graduate student, Department of Industrial Chemistry

Table 1 Bromination of Phenols by Use of Benzyltrimethylammonium Chlorobromate(1-)

Substrate(I)	Product(II)	Molar ratio (BTMA ClBr <sub>2</sub> /I)	Reaction time(min)	Yield <sup>a)</sup> %	Mp m/°C	
					found	reported
1 <sup>b)</sup> 	 2)	3.1	20	93	90-91	95 <sup>4)</sup>
2 	 3)	2.1	1	96	60	64 <sup>5)</sup>
3 	 3)	3.1	30	95	82	81-82 <sup>5)</sup>
4 	 2)	2.1	10	96	46-48	49 <sup>6)</sup>
5 	 2)	2.1	5	94	70-71	70-71 <sup>7)</sup>
6 	 2)	2.1	6	94	69-70	67-68
7 	 3)	2.1	7	93	79-80	79-80 <sup>8)</sup>
8 	 3)	1.1	1	96	78-79	79.5 <sup>9)</sup>
9 	 3)	2.1	7	94	39-40	39-40 <sup>10)</sup>
10 	 3)	3.1	5	92	165	165 <sup>11)</sup>
11 	 2)	2.1	10	95	63-64	64-65 <sup>12)</sup>
12 <sup>b)</sup> 	 2)	3.1	5	94	104-105	104 <sup>13)</sup>
13 <sup>b)</sup> 	 2)	2.1	5	96	75	76 <sup>14)</sup>
14 <sup>b)</sup> 	 2)	3.1	5	96	103-104	105-106 <sup>15)</sup>
15 <sup>b)</sup> 	 2)	2.1	5	96	91-92	92 <sup>16)</sup>

Continued

16 <sup>b)</sup>			2.1	5	82	89	95 <sup>4)</sup>
17 <sup>b)</sup>			3.1	5	90	112	111 <sup>17)</sup>
18 <sup>b)</sup>			2.1	5	92	93	95 <sup>4)</sup>
19 <sup>b)</sup>			2.1	10	94	134	134 <sup>18)</sup>
20 <sup>b)</sup>			1.1	30	94	67-68	69 <sup>19)</sup>
21 <sup>b)</sup>			2.1	10	95	116-118	118 <sup>20)</sup>
22 <sup>b)</sup>			3.1	30	89	89-90	89-90 <sup>21)</sup>
23 <sup>b)</sup>			2.1	5	96	145.5	144 <sup>22)</sup>
24 <sup>b)</sup>			2.1	5	94	222	228 <sup>23)</sup>
25 <sup>b)</sup>			2.1	5	91	152	149 <sup>24)</sup>
26 <sup>b)</sup>			2.1	7	93	97-98	101 <sup>24)</sup>
27 <sup>b)</sup>			3.1	20	93	146	146-147 <sup>25)</sup>
28 <sup>b)</sup>			2.1	5	91	122	125 <sup>26)</sup>
29 <sup>b)</sup>			2.1	5	95	108	108 <sup>26)</sup>
30			3.1	1	94	111	112 <sup>27)</sup>
31			2.1	1	93	101	102 <sup>28)</sup>

Continued

32			3.1	1	94	97	98 <sup>29)</sup>
33 <sup>b)</sup>			4.1	3	95	201-202	200-201 <sup>30)</sup>

a) Yield of isolated product. b) CaCO<sub>3</sub> powder was used.

phenol(I-1) with 3 equiv. of these reagents, BTMA ClBr<sub>2</sub>, BTMA Br<sub>3</sub>, and TBA Br<sub>3</sub>, in dichloromethane-methanol at room temperature for twenty minutes, one hours<sup>2)</sup>, and two hours<sup>3)</sup>, respectively. That is, we can emphasize that BTMA ClBr<sub>2</sub> is the most effective brominating agent for I among these reagents.

Furthermore, it turned out that polybromophenols bearing electron-attracting group such as nitro-, carboxy- or alkoxy-carbonyl group were easily obtained by use of BTMA ClBr<sub>2</sub>.

### Experimental

**Benzyltrimethylammonium Chlorobromate(1-).** To a solution of bromine (15.98g, 0.1mol) in dichloromethane (100ml) was added dropwise a solution of benzyltrimethylammonium chloride (18.57g, 0.1mol) in water (100ml) under stirring at room temperature. After the mixture was stirred for 30min, the dichloromethane layer was separated and dried with magnesium sulfate, and then evaporated *in vacuo* to give the residue which was recrystallized from dichloromethane-ether (10:1) affording BTMA ClBr<sub>2</sub> as stable orange crystals; yield 24.50g (71%); mp 101-102°C. Found: C, 34.88; H, 4.63; N, 4.01; ClBr<sub>2</sub>, 56.31%. Calcd for C<sub>10</sub>H<sub>16</sub>NClBr<sub>2</sub>: C, 34.76; H, 4.67; N, 4.05; ClBr<sub>2</sub>, 56.51%.

#### 2, 4, 6-Tribromophenol(II-1), Typical procedure.

To a solution of phenol (0.50g, 5.51mmol) in dichloromethane (50ml)-methanol (20ml) was added BTMA ClBr<sub>2</sub> (5.69g, 16.47mmol) and calcium carbonate powder (2g) at room temperature. The mixture was stirred for 20 min until a fading of the orange color took place. The solid calcium carbonate was filtered off, the filtrate was concentrated and to the obtained residue was added water (20ml). The mixture was extracted with ether (40ml x 4). The ether layer was then dried with magnesium sulfate and evaporated *in vacuo* to give a residue which was recrystallized from methanol-water (1:3) affording 2, 4, 6-tribromophenol (II-1) as colorless crystals; yield 1.64g (93%); mp 91-92°C (Lit.,<sup>4)</sup> mp 95°C).

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