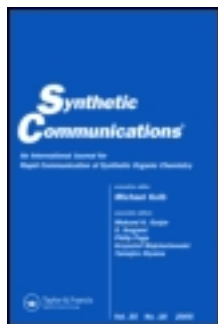


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**FACILE SYNTHESIS OF  
( $\omega$ -BROMOALKYL)TRIMETHYLAMMONIUM  
BROMIDES**

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**Abstract.** Reaction of a 1, $\omega$ -dibromoalkane with trimethylamine in THF at room temperature precipitates the corresponding ( $\omega$ -bromoalkyl)trimethylammonium bromide to cleanly form the mono-substituted product in the absence of the bis-quat salt.

For use in the preparation of bifunctional anion-exchange resins for the sorption of plutonium(IV) from concentrated nitric acid solutions by alkylation of poly(4-vinylpyridine),<sup>1</sup> a viable synthetic route to ( $\omega$ -bromoalkyl)trimethylammonium salts was needed.

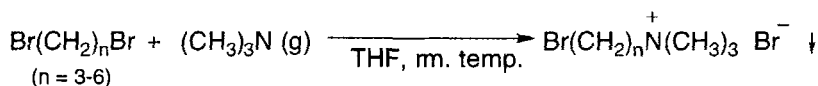
For reactions of 1, $\omega$ -dibromoalkanes with trimethylamine in benzene, toluene or ethanol, formation of both mono- and disubstituted products was reported,<sup>2-4</sup> even when a large excess of the 1, $\omega$ -dibromoalkane was utilized.<sup>3</sup> Formation of the bis-

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quat salts as by-products was confirmed in our laboratories by  $^1\text{H}$  NMR spectroscopy of the crude reaction products.

A search was undertaken for a solvent in which the ( $\omega$ -bromoalkyl)-trimethylammonium bromide would precipitate from solution as it was formed and thereby prevent further reaction. We now report that the reaction of a 1, $\omega$ -dibromoalkane with trimethylamine in THF at room temperature produces cleanly the corresponding ( $\omega$ -bromoalkyl)trimethylammonium bromide in high yield and free from bis-quat salt contamination when the alkylene unit contains 3-6 methylene groups.



In the reaction procedure, trimethylamine gas was slowly bubbled into a stirred THF solution of the 1, $\omega$ -dibromoalkane for a few hours at room temperature. The reaction flask was then stoppered and the reaction mixture was stirred for 1-3 days at room temperature. The pure ( $\omega$ -bromoalkyl)trimethylammonium bromide product was obtained good-to-excellent yield (usually 90 % or greater) by filtration of the reaction mixture. Results for reactions of 1, $\omega$ -dibromoalkanes containing 3-6 methylene groups, as well as for bis(2-bromoethyl) ether and for *cis*- and *trans*-1,4-dichloro-2-butene, are presented in Table 1. The capability for scale-up of the reaction procedure was demonstrated by conversion of 1.05 moles of 1,5-dibromopentane into (5-bromopentyl)trimethylammonium bromide in nearly quantitative yield.  $^1\text{H}$  NMR spectral data for the seven mono-quat salts and elemental analysis results for the previously unknown compounds are recorded in Table 2.

Table I. Reactions of 1, $\omega$ -Dibromoalkanes with Trimethylamine in THF.

n of $\text{Br}(\text{CH}_2)_n\text{Br}$	scale (mmol)	time		yield (%)	mp/lit mp
		bubbling	reaction		
3	120	2 hr	2 days	90	$\frac{217-220}{205}$ (dec) <sup>2</sup>
4	120	4 hr	3 days	93	$\frac{127-129}{131-134}$ <sup>4</sup>
5	1,050	20 hr <sup>a</sup>	3 days <sup>a</sup>	97	$\frac{144-146}{133-136}$ <sup>2</sup>
6	20	2.5 hr	1 day	78	$\frac{105-107}{106-108}$ <sup>2</sup>
b	40	3 hr	1 day	98	113-115
c	143	2 hr	1 day	95	176-178
d	8	0.5 hr	6 hr	95	185-188

<sup>a</sup>Cumulative times for a large-scale reaction (see Experimental Section). <sup>b</sup>Bis(2-bromoethyl) ether. <sup>c</sup>*cis*-1,4-Dichloro-2-butene. <sup>d</sup>*trans*-1,4-Dichloro-2-butene.

For reactions with 1,7-dibromoheptane and 1,8-dibromooctane, the filtered reaction product was found to be a mixture of the mono-quat salt contaminated with the corresponding bis-quat product. Apparently the greater lipophilicity of these mono-substitution products allows further reaction to become competitive with their precipitation.

Although reaction of *trans*-1,4-dibromo-2-butene produced only the bis-quat product due the higher reactivity of the allylic bromide system, reactions of *cis*- and *trans*-1,4-dichloro-2-butene cleanly gave the mono-quat products. The reaction of *trans*-1,4-dichloro-2-butene was observed to be much faster, presumably due to greater steric hindrance in the *cis*-isomer.

Table 2.  $^1\text{H}$  NMR Spectra and Elemental Analysis Data

no. of $\text{CH}_2$	groups	$^1\text{H}$ NMR ( $\text{CDCl}_3$ ): $\delta$ / Elemental Analysis
3		2.38-2.52 (m, 2H), 3.53 (s, 9H), 3.55 (t, $J=11.9$ Hz), H), 3.84-3.92 (m, 2H)
4		1.92-2.04 (m, 4H), 3.45-3.58 (m, 11H), 3.78-3.84 (m, 2H)
5		1.58-1.62 (m, 2H), 1.77-2.04 (m, 4H), 3.45 (t, $J=4$ Hz, 2H), 3.49 (s, 9H), 3.66-3.75 (m, 2H)
6		1.44-1.54 (m, 4H), 1.73-1.92 (m, 4H), 3.43 (t, $J=6.5$ Hz, 2H), 3.49 (s, 9H), 3.63-3.72 (m, 2H).
a		3.56 (m, 11H), 3.90 (m, 2H), 4.05 (s, 4H) / Anal Calcd for $\text{C}_7\text{H}_{17}\text{Br}_2\text{NO}$ : C, 28.89; H, 5.89. Found: C, 29.28; H, 5.83.
b		3.47 (s, 9H), 4.53 (dd, $J=8.2$ and $0.5$ Hz, 2H), 5.81 (m, 1H), 6.30 (m, 1H) / Anal Calcd for $\text{C}_7\text{H}_{15}\text{Cl}_2\text{N}$ : C, 45.65; H, 8.15. Found: C, 45.28; H, 8.33.
c		3.43 (s, 9H), 4.16 (dd, $J=5.8$ and $1.0$ Hz, 2H), 4.57 (d, $J=7.6$ Hz), 2H), 6.00 (m, 1H) / Anal Calcd for $\text{C}_7\text{H}_{15}\text{Cl}_2\text{N}$ : C, 45.65; H, 8.15. Found: C, 45.68; H, 8.02.

<sup>a</sup>(5-Bromo-3-oxapentyl)trimethylammonium bromide. <sup>b</sup>*cis*-1-Chloro-4-trimethylammonio-2-butene bromide. <sup>c</sup>*trans*-1-Chloro-4-trimethylammonio-2-butene bromide.

Use of *tert*-butyl methyl ether, an alternative ether solvent, gave a mixture of mono- and bis-quat products in the reaction of 1,5-dibromopentane with trimethylamine.

### Experimental Section

All reactants were commercially available and used as received. THF was distilled from Na/benzophenone. <sup>1</sup>H NMR spectra were measured at 200 MHz in CDCl<sub>3</sub> with TMS as internal standard. Elemental analysis was performed by Desert Analytics Laboratory of Tuscon, Arizona.

**Synthesis of (4-Bromobutyl)trimethylammonium Bromide.** (Typical Procedure) In a fume hood, 26.2 g (120 mmol) of 1,4-dibromobutane, 250 mL of dry THF and a magnetic stirring bar were placed in a 1000-mL, three-necked flask. Into one side neck of the flask was inserted a glass tube with a drawn tip which extended below the surface of the solution. To the second neck was attached a CaCl<sub>2</sub> drying tube and the third neck was closed with a stopper. Trimethylamine gas was introduced into the solution at a rate of 12 mL/min for 4 hr at room temperature. The trimethylamine addition and drying tubes were replaced with stoppers and the reaction mixture was stirred for 24 hr. The precipitate was filtered to give 32.0 g (93%) of (4-bromobutyl)trimethylammonium bromide.

**Synthesis of (5-Bromopentyl)trimethylammonium Bromide.** (Large-scale Reaction) In a fume hood, 250 g (1.05 mol) of 1,5-dibromopentane, 1.50 L of dry THF and a magnetic stirring bar were placed in a 3-L, three-necked flask equipped as described above. Trimethylamine gas was introduced into the solution at a rate of 12 mL/min for 7 hr at room temperature. The trimethylamine addition and drying tubes were replaced with stoppers and the reaction mixture was stirred for 24 hr. The precipitate was filtered and the filtrate was returned to the flask, the trimethylamine addition and CaCl<sub>2</sub> drying tubes were reattached and trimethylamine

was added as before for another 7-hr period. The trimethylamine addition and drying tubes were replaced with stoppers and the reaction mixture was stirred for 24 hr. The precipitate was filtered and the filtrate was returned to the flask once again. Following trimethylamine introduction for another 7 hr at room temperature and stirring for 24 hr, the precipitate was filtered. The combined precipitates gave 294.2 g (97 %) of (5-bromopentyl)trimethylammonium bromide.

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