

# Stereoselective Bromination Reactions Using Tridecylmethylphosphonium Tribromide in a “Stacked” Reactor

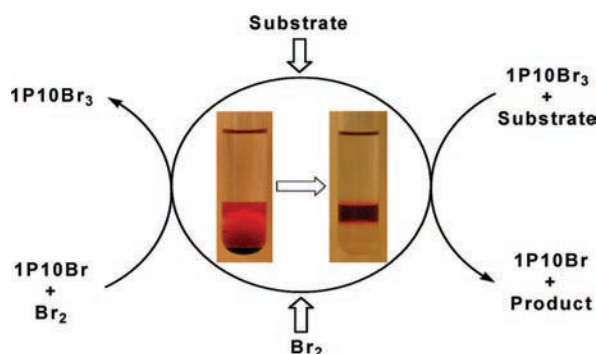
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## ABSTRACT



A new reagent, tridecylmethylphosphonium tribromide, and new procedures for bromination reactions of unsaturated substrates (including one that allows several substrates to be reacted in sequence) are described. The procedures exploit the diffusion of components and the densities and immiscibilities of layers, including a fluoruous “spacer” layer, within a reaction vessel. The stereoselectivities achieved in the reactions are superior in some cases to those found with other brominating reagents.

Bromination reactions of unsaturated molecules involving additions or electrophilic substitutions are common in organic

synthesis. Typically, they are performed in batch processes by dissolving the substrate and the brominating reagent in a common solvent. However, the most common of these reagents, bromine, is difficult to manipulate due to its toxicity, corrosiveness, and high vapor pressure. Although several other brominating reagents<sup>1–3</sup> have been introduced to minimize these problems, new reagents are needed for specific applications, especially if they reduce the environmental impact of the reactions.

Here, we describe how a new ionic liquid, tridecylmethylphosphonium tribromide (**1P10Br<sub>3</sub>**), can be used in bromination processes, including one in which several reactions are conducted sequentially, without classical workup pro-

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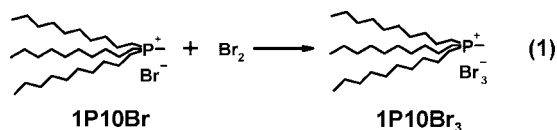
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cedures. **1P10Br<sub>3</sub>** is made by reaction of tridecylmethylphosphonium bromide (**1P10Br**)<sup>4</sup> with molecular bromine (eq 1), and it is replenished in situ during the brominations (Scheme S1 of Supporting Information).



The tribromide anion, Br<sub>3</sub><sup>-</sup>, is very stable when neat<sup>5</sup> or dissolved in aprotic solvents<sup>6</sup> and is a safer and more easily handled reagent because it lacks the volatility of molecular bromine. Its quaternary ammonium salts can effect bromination reactions in solutions or as solids,<sup>2,3</sup> and they have been used to catalyze several acetalization and pyranylation reactions.<sup>7</sup> The results presented here demonstrate how the larger size of P<sup>+</sup> than N<sup>+</sup>, its lower binding energy with anions,<sup>8</sup> and the broadened liquid phase range of **1P10Br<sub>3</sub>**<sup>4</sup> may be exploited to brominate a wide variety of substrates.

**Characterization of 1P10Br<sub>3</sub>.** Both the larger size and more delocalized electrons of the Br<sub>3</sub><sup>-</sup> anion contribute to the drastically lower melting temperature of **1P10Br<sub>3</sub>** (−19.8 to −26.3 °C upon cooling by optical microscopy and DSC; Figure S1-A of Supporting Information) than of **1P10Br** (98.8–100.7 °C<sup>4g</sup>).

The X-ray diffractogram of **1P10Br<sub>3</sub>** in the liquid phase at room temperature contains a weak, low-angle peak corresponding to  $d = 18.2 \text{ \AA}$  from residual molecular packing of tridecylmethylphosphonium ions<sup>4g</sup> (Figure S1-B of Supporting Information). The broad peak centered near 22° (corresponding to a Bragg distance of  $\sim 4.0 \text{ \AA}$ ) is attributed to interchain interactions from London dispersion forces.<sup>9</sup>

**1P10Br<sub>3</sub> as a Brominating Reagent.** **1P10Br<sub>3</sub>** is insoluble in long alkanes. Its red color was slowly lost as bromination occurred when it was added to a solution of hexadecane containing an unsaturated substrate. Because no bromine was

detected by UV–vis spectroscopy in a neat upper hexadecane layer that was in contact with **1P10Br<sub>3</sub>** for two weeks, reaction with substrates is proposed to occur only at the **1P10Br<sub>3</sub>**–hexadecane layer interface. Thus, the careful control of both temperature and addition of molecular bromine, which are needed to avoid undesirable side reactions in solution-phase brominations with Br<sub>2</sub>,<sup>10</sup> is not necessary here. Table 1 summarizes the yields and distributions of products with **1P10Br<sub>3</sub>** as the brominating reagent using different protocols.

**Batch Reactions (Two-Layer Systems).** Typically, a vessel was loaded with **1P10Br<sub>3</sub>** and an upper layer of hexadecane with dissolved substrate, capped to avoid evaporation or introduction of moisture, and left undisturbed until workup. To increase somewhat the rates of these brominations, a slight molar excess of **1P10Br<sub>3</sub>** was added. When the brominated products were solids, they were easily isolated by gravity filtration followed by washing with hexane in which **1P10Br** is soluble. The **1P10Br** is easily recovered by evaporation of the hexane, and **1P10Br<sub>3</sub>** can be regenerated by addition of more bromine. In those cases where the products are soluble in hexadecane, the upper layer can be removed with a pipet, followed by one of a variety of separation techniques that depends on the relative boiling points or column elution characteristics of the components. A detailed description of the physical isolation of a liquid and a solid bromination product is provided in the Supporting Information file.

The bromination of *cis*-stilbene in hexadecane by **1P10Br<sub>3</sub>** was almost exclusively *syn* (producing *meso*-1,2-dibromo-1,2-diphenylethane) and in a reasonable chemical yield (entry 3 in Table 1). No *meso*⇌*d,l* isomerization of product was observed under these reaction conditions. Reaction with **1P10Br<sub>3</sub>** dissolved in 1,2-dichloroethane or with bromine in hexadecane (entry 3) was almost exclusively *anti*, as expected,<sup>11</sup> providing the *d,l* stereoisomer. The Br<sub>3</sub><sup>-</sup> reagents with ammonium counterions also yielded exclusively or predominantly the isomer from *anti* addition either in solvent-free<sup>3a</sup> or solution reactions.<sup>2b,6</sup> The observation of *syn* bromination at a high *cis*-stilbene concentration (ca. 0.3 M) in hexadecane appears to be unprecedented. In 1,2-dichloroethane solutions, the maximum *syn/anti* ratio, 9/1, has been reported at the lowest *cis*-stilbene ( $\sim 10^{-5} \text{ M}$ ) and the highest Br<sub>2</sub> ( $\sim 10^{-3} \text{ M}$ ) concentrations employed.<sup>12</sup> We conjecture that the *syn* addition with **1P10Br<sub>3</sub>** is related to the manner in which stilbene molecules sit on the surface of the **1P10Br<sub>3</sub>** layer. However, no *syn* addition to *trans*-stilbene was observed with **1P10Br<sub>3</sub>**, although it does occur in solution!<sup>12</sup> More experimentation will be required to understand the mechanisms responsible for these results.

**Batch Reactions (Four-Layer System).** A bromination system employing four separate liquid layers was also devised. Examples employing **1P10Br<sub>3</sub>** and **1P10Br** as the

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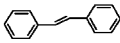
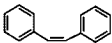

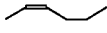


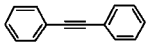

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**Table 1.** Product Yields and Distributions of *syn/anti* Dibrominated Addition (or Other) Products for Reactions of Various Substrates at Room Temperature Using Three Experimental Protocols (See Supporting Information file for product NMR spectra)

entry	substrate	4 layers (substrate in hexadecane/ <b>1P10Br<sub>3</sub></b> /perfluorohexane/Br <sub>2</sub> )		2 layers (substrate in hexadecane/ <b>1P10Br<sub>3</sub></b> )		stirred solution (substrate and Br <sub>2</sub> in hexadecane)	
		yield/time	<i>anti/syn</i> <sup>a</sup>	yield/time	<i>anti/syn</i> <sup>a</sup>	yield/time	<i>anti/syn</i> <sup>a</sup>
1				61%/2 d 92%/6 d 99%/12 d	100:0 100:0 100:0	100%/30 min	100:0
2		84%/10 d	100:0	78%/10 d	100:0	100%/30 min	99:1
3		57%/10 d 53%/15 d	6:94 <sup>b</sup> 10:90 <sup>c</sup>	51%/10 d	2:98 <sup>b</sup>	100%/30 min	95:5
4		100%/5 d 100%/10 d	92:8 93:7 <sup>c</sup>	100%/10 d	95:5	100%/30 min	100:0
5		100%/5 d 100%/10 d	85:15 78:22 <sup>c</sup>	100%/10 d	72:28	100%/30 min	100:0
6		100%/10 d	96:4	100%/10 d	100:0	100%/30 min	68:32
7		7%/20 d	100:0 <sup>d</sup>	0%/20 d 0%/30 d <sup>e</sup>		42%/20 d	100:0 <sup>f</sup>
8		78%/20 d <sup>g</sup>	100:0 <sup>h</sup>	70%/20 d	100:0 <sup>h</sup>	92%/5 h <sup>g</sup>	84:16 <sup>h</sup>
9		67%/20 d <sup>g</sup>	50:44:6 <sup>i</sup>	15%/12 d 15%/30 d <sup>c</sup>	100:0 <sup>j</sup> 100:0 <sup>j</sup>	87%/20 d <sup>g</sup>	93:0:7 <sup>i</sup>

<sup>a</sup> Based on product stereochem for entries 1–8. <sup>b</sup> Average of two experiments. <sup>c</sup> From sequential bromination experiments; see below. <sup>d</sup> Plus 36% 9-bromophenanthrene. <sup>e</sup> Stirred the last 2 days. <sup>f</sup> Plus 32% 9-bromophenanthrene. <sup>g</sup> 1.0 equiv of Br<sub>2</sub>. <sup>h</sup> *trans*-1,2-Dibromo-1,2-diphenylethene:1,1,2,2-tetrabromo-1,2-diphenylethane. <sup>i</sup> 4-Bromoanisole:2,4-dibromoanisole:2,4-dibromophenol (4 layer) or 4-bromoanisole:2,4-dibromoanisole:2-bromoanisole (Br<sub>2</sub>/hexadecane). <sup>j</sup> 4-Bromoanisole:2,4-dibromoanisole.

initial reagent are shown in Figure 1.<sup>13</sup> Both permit consumed **1P10Br<sub>3</sub>** (i.e., **1P10Br**) to be regenerated in situ without the unsaturated substrates coming into direct contact with molecular bromine. Our design, based on solubilities and densities, is an extension of the clever use of perfluorohexane ( $d = 1.67$  g/mL) by Ryu, Curran, and co-workers<sup>14</sup> and Jana and Verkade<sup>15</sup> as a moderating layer in “phase-vanishing” bromination reactions. In our case, perfluorohexane separates the bromine layer at the bottom ( $d = 3.12$  g/mL) from the **1P10Br<sub>3</sub>** ionic liquid layer ( $0.77$  g/mL  $< d < 1.67$  g/mL) and hexadecane/substrate top layers ( $d = 0.77$  g/mL). The rate of bromine transport can be controlled by the thicknesses of the perfluorohexane and phosphonium salt layers or by immersing the bromine and perfluorohexane layers in a cold bath.<sup>16</sup>

(13) We have not observed large differences in the outcomes of reactions conducted with the two salts. The *syn/anti* ratio for products from *cis*-stilbene was 97/3 when **1P10Br** was the initial salt in contact with the hexadecane layer (as compared to 94/6 reported in Table 1 using **1P10Br<sub>3</sub>**). However, use of **1P10Br<sub>3</sub>** is recommended in general because, in some cases, bromine that diffuses from below may react more slowly with the solid **1P10Br** than it diffuses through the phosphonium layer and reacts with molecules in the upper hexadecane layer.

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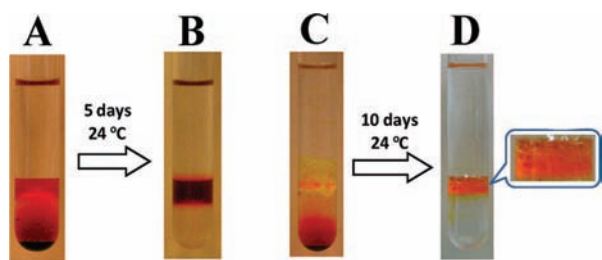
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Perfluorohexane, being heavier than **1P10Br<sub>3</sub>** or **1P10Br** but lighter than liquid bromine and immiscible in both, serves as a membrane to regulate diffusion of bromine<sup>14</sup> into the **1P10Br/1P10Br<sub>3</sub>** layer: **1P10Br<sub>3</sub>** that is lost during reaction with substrate is replenished; the liquid nature of the phosphonium phase is maintained; and the top layer, containing hexadecane and a substrate, continues to be exposed to an adequate amount of **1P10Br<sub>3</sub>**. As will be discussed later, this system is also amenable to conducting sequential bromination reactions without dismantling it between changes of substrates.

Tribromide anions can associate with one additional Br<sub>2</sub> molecule to form Br<sub>5</sub><sup>-</sup>.<sup>6</sup> Such a species, **1P10Br<sub>5</sub>**, may be present here, and its presence is indicated by the red layer in Figure 1B at the end of the reaction (in which an excess of molecular bromine was added): the bromine layer has disappeared completely; the perfluorohexane and hexadecane layers are colorless; and even with the 100% product yield found (entry 4 in Table 1), there remain 1.2 molecules of Br<sub>2</sub> per molecule of **1P10Br**.<sup>17</sup>

Product ratios are based on areas of diagnostic peaks in <sup>1</sup>H NMR spectra of reaction mixtures (see the Supporting Information file). The results indicate that the use of **1P10Br<sub>3</sub>**

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**Figure 1.** Four-layer brominating systems consisting of (from top to bottom): (A) *trans*-2-hexene (72 mg, 0.86 mmol) in 2.1 mL of hexadecane, **1P10Br<sub>3</sub>** (335 mg, 0.47 mmol; 5 mm in layer thickness), perfluorohexane (1.42 g; 11 mm layer thickness), and bromine (163 mg, 1.02 mmol), and (C) *cis*-stilbene (135 mg, 0.75 mmol) in 3.2 mL of hexadecane, small solid pieces of **1P10Br** (412 mg, 0.75 mmol; 5 mm in layer thickness), perfluorohexane (2.25 g; 13.5 mm layer thickness), and bromine (120 mg, 0.75 mmol). The interior diameters of the round tube in **A/B** and **C/D** are 10.5 mm (87 mm<sup>2</sup> surface area) and 11.5 mm (104 mm<sup>2</sup> surface area), respectively. Initial stages of the reaction in **A** and **C** show that bromine has already begun to diffuse through the perfluorohexane layer (red gradient). **B** and **D** show the loss of the bromine layer with time and residual bromine in the phosphonium layer. Note the crystals of 1,2-dibromo-1,2-diphenylethane atop the phosphonium salt layer in the expanded view of **D**.

has some distinct stereochemical advantages in some cases but is not the method of choice in others due to lower yields (entry 7) or longer periods needed to obtain high product yields (entries 1, 4, and 5).

However, brominations using **1P10Br<sub>3</sub>** are the most stereoselective of the methods examined for *trans*-stilbene (entry 2) and acenaphthylene (entry 6) and the most chemoselective for diphenylacetylene (entry 8). Interestingly, bromination of anisole (entry 9) using the two-layer system with **1P10Br<sub>3</sub>** resulted in exclusive *para*-substitution, albeit in a low yield. Surprisingly, the total yield of bromination products is improved significantly by employing the four-layer system, but it was attended by formation of some 2,4-dibromoanisole and 2,4-dibromophenol (from disubstitution and ether cleavage).

**Sequential Brominations (Four-Layer System).** In a demonstration of principle, we have brominated *trans*-2-hexene, *cis*-2-hexene, and *cis*-stilbene in sequence without disassembling the reactor (Figure S2<sup>18</sup> and Supporting

(17) We have not compared as yet the regio- and stereoselectivities of brominations using **1P10Br<sub>3</sub>** and **1P10Br<sub>5</sub>**. The configurations of our systems strongly suggest that **1P10Br<sub>3</sub>** is the dominant brominating agent in the work reported here.

(18) A slightly more sophisticated apparatus, which allows for the direct addition of bromine to the bottom layer and direct removal of the hexadecane layers, has been designed, and results from experiments in which it is used will be reported in the future.

Information file). After each bromination, the hexadecane layer (containing the soluble products) was removed with a pipet. More bromine was added through a sidearm with a column of perfluorohexane when a new substrate in hexadecane was added above the phosphonium salt layer. Because the bromination products from *cis*-stilbene are insoluble in hexadecane, it was reacted last. Results from these and from the two-phase batch system for the same substrates are very similar (Table 1). At the end of the sequence, there was no indication of degradation of the phosphonium salt; the bromination system is a rechargeable “green” reactor.

In conclusion, we have used a new ionic liquid, **1P10Br<sub>3</sub>**, to brominate a variety of substrates using three reactor conditions, including two that depend on the densities and immiscibilities of four species. The reactions require mild conditions and, in some cases, are more stereoselective than other reagents. Sequential brominations of substrates within one reactor have been demonstrated as well. Thus far, we have not attempted to optimize the bromination conditions. Clearly, it should be possible to increase the rates at which the reactions occur in two-layer batch reactions by rapidly stirring or sonicating the mixtures. The rates of conversions of reactions in the four-layer systems can be modulated as well using variables, such as temperature, interfacial surface areas, layer thicknesses, and even stirring within single layers. Other possible variables to be explored in future work include alteration of the structure of the phosphonium cation,<sup>4</sup> performing iodinations and chlorinations with phosphonium triiodides<sup>19</sup> and trichlorides,<sup>20</sup> and substituting other liquids that dissolve brominated products better than hexadecane.

**Acknowledgments.** We are grateful to the U.S. National Science Foundation for financial support of this research and to Dr. Al Robertson of Cytec Corporation for supplying the precursor tri-decylphosphine.

**Supporting Information Available:** Instrumentation, sample preparations, NMR spectra of brominated products and procedures for their isolation, phase characterizations of **1P10Br<sub>3</sub>** by differential scanning calorimetry and X-ray diffractometry, and experimental procedures for different bromination methods. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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