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# QUATERNARY AMMONIUM BROMIDE CATALYZED CHLORIDE FOR BROMIDE REDISTRIBUTIONS BETWEEN CARBON OF ALKYL HALIDES AND TIN OF TRI-n-BUTYLTIN HALIDES

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## Summary

Quaternary ammonium bromides have been found to strongly catalyze reversible chloride for bromide substitution reactions by tri-n-butyltin chloride on benzyl bromide and n-octyl bromide. However, they have only a small effect upon the rate of the corresponding reaction with benzhydryl bromide. It is suggested that the catalytic effect involves initial coordination of bromide ion with tri-n-butyltin chloride to form a nucleophilic anionic complex containing pentavalent tin which is reactive for backside displacements at carbon of sterically unhindered alkyl halides. No catalytic effects could be demonstrated, however, for ligands such as pyridine or *N,N*-dimethylformamide which could potentially form zwitterionic complexes with tri-n-butyltin chloride.

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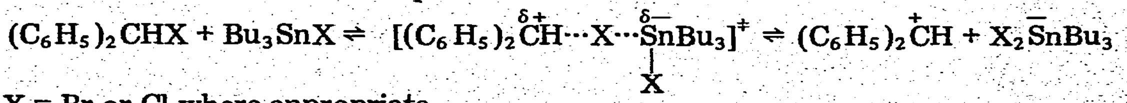
## Introduction

We recently reported [1] a new halogen redistribution reaction between carbon of alkyl halides and tin of tri-n-butyltin halides. For example, when benzhydryl bromide is heated at 50°C with tri-n-butyltin chloride in an initial 1 : 1 mole ratio for 2 hours in the absence of a solvent, an equilibrium mixture is obtained containing 70% benzhydryl chloride and tri-n-butyltin bromide and 30% benzhydryl bromide and tri-n-butyltin chloride.

$$(C_6H_5)_2CHBr + Bu_3SnCl \overset{K_{eq} = 5.9}{\rightleftharpoons} (C_6H_5)_2CHCl + Bu_3SnBr$$

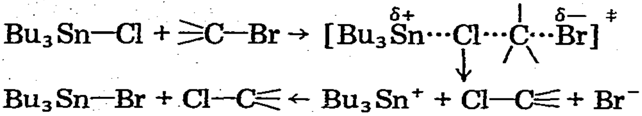
Our investigations of the mechanism of this reaction [1] showed that it involves rate-determining tri-n-butyltin halide assisted benzhydryl halide ionization for both the forward and reverse processes.



$$(C_6H_5)_2CHX + Bu_3SnX \rightleftharpoons [(C_6H_5)_2\overset{\delta+}{C}H\cdots X\cdots \underset{\displaystyle X}{\overset{\delta-}{S}}nBu_3]^{\ddagger} \rightleftharpoons (C_6H_5)_2\overset{+}{C}H + X_2\overset{-}{S}nBu_3$$

X = Br or Cl where appropriate

Whereas the chloride for bromide substitution reaction with benzhydryl bromide occurs readily, the corresponding reaction of tri-n-butyltin chloride with benzyl bromide proceeds very slowly even at 150° C. Also, with n-octyl bromide no detectable reaction is observed after 5 days at 100° C. These results are not surprising, however, since ionizations of benzyl bromide and especially of n-octyl bromide in the low ionizing power, neat mixtures of reactants would be expected to be very slow. Also, an alternative possibility of direct $S_N2$ type backside displacements on these bromides by tri-n-butyltin chloride should not proceed readily since the energetically unfavorable [2] formation of a tri-n-butyltin cation intermediate would appear to be required.



$$\mathrm{Bu_3Sn{-}Cl} + \geqslant\mathrm{C{-}Br} \rightarrow [\mathrm{Bu_3\overset{\delta+}{Sn}\cdots Cl\cdots \overset{|}{\underset{/\,\backslash}{C}}\cdots \overset{\delta-}{Br}}]^{\ddagger}$$
$$\downarrow$$
$$\mathrm{Bu_3Sn{-}Br} + \mathrm{Cl{-}C}\leqslant\ \leftarrow \mathrm{Bu_3Sn^+} + \mathrm{Cl{-}C}\leqslant + \mathrm{Br^-}$$

The low reactivities of alkyl halides such as the benzyl and n-octyl bromides, which do not very readily undergo ionization, severely limit the utility of the halogen redistribution process. However, theoretical consideration suggested to us that suitable Lewis bases might strongly catalyze their reactions. The results of our investigations into this interesting possibility are described below.

## Results and discussion

As we explained above, trialkyltin halides would not be expected to behave as good nucleophiles for backside displacements at carbon of alkyl halides. On the other hand, we reasoned that complexes of trialkyltin halides with Lewis bases [3] might be highly reactive in such reactions, especially if they are of the anionic type. This is because their reactions can be formally written without having to place a positive charge on tin. Thus, addition of suitable Lewis bases might strongly catalyze the halogen redistribution reactions of trialkyltin halides with those alkyl halides which are known to be reactive toward nucleophilic backside substitutions, but which are unreactive in the trialkyltin halide promoted ionization process.

It was gratifying to observe that the results of tests carried out using bromide ion as the Lewis base were in complete accord with our predictions. As is shown by the data in Table 1, the addition of catalytic amounts of tetra-n-butylammonium bromide caused large accelerations in the rates of reaction of tri-n-butyltin chloride with benzyl bromide and n-octyl bromide, but had only a small rate accelerating effect on the corresponding reaction of benzhydryl bromide. Also, in the benzyl bromide reaction, *N*-benzylpyridinium bromide was found within experimental error to exhibit an identical rate accelerating affect to that of tetra-n-butylammonium bromide. Finally, it was shown that the tetra-n-butylammonium and *N*-benzylpyridinium cationic species were unchanged during the course of the reactions.

The small, essentially linear, rate accelerations caused by added tetra-n-butylammonium bromide on the reactions of benzhydryl bromide with tri-n-butyltin chloride can be explained as being due to a salt effect [4] on the rate of tri-n-butyltin halide promoted benzhydryl bromide ionization [1]. However, it is

TABLE 1

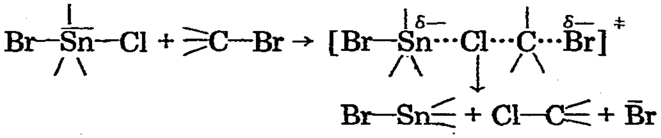
REACTIONS OF VARIOUS ALKYL BROMIDES WITH TRI-n-BUTYLTIN CHLORIDE, NEAT, IN 1 : 1 MOLAR RATIOS IN THE ABSENCE AND PRESENCE OF ADDED QUATERNARY AMMONIUM BROMIDES

| RBr | Additive | [Additive] (*M*) | Temp. (°C) | Time for 30% RCl formation (min) | RCl [a] (%) at equil. |
|---|---|---|---|---|---|
| $(C_6H_5)_2CHBr$ [b] | None | — | 40 ± 1 | 45 ± 5 | 71 ± 1 |
| $(C_6H_5)_2CHBr$ | $Bu_4NBr$ | 0.062 | 40 ± 1 | 37 ± 3 | 72 ± 1 |
| $(C_6H_5)_2CHBr$ | $Bu_4NBr$ | 0.124 | 40 ± 1 | 28 ± 2 | 70 ± 1 |
| $(C_6H_5)_2CHBr$ | $Bu_4NBr$ | 0.180 | 40 ± 1 | 24 ± 2 | 68 ± 1 |
| $(C_6H_5)_2CHBr$ | $Bu_4NBr$ | 0.238 | 40 ± 1 | 18 ± 2 | 68 ± 1 |
| $C_6H_5CH_2Br$ [c] | None | — | 50 ± 0.5 | No reaction after 4000 min | |
| $C_6H_5CH_2Br$ | $Bu_4NBr$ | 0.134 | 50 ± 0.5 | 130 ± 10 | 64 ± 1 |
| $C_6H_5CH_2Br$ | $Bu_4NBr$ | 0.255 | 50 ± 0.5 | 60 ± 5 | 64 ± 1 |
| $C_6H_5CH_2Br$ | $C_5H_5NBzBr$ [d] | 0.132 | 50 ± 0.5 | 140 ± 10 | 65 ± 1 |
| $C_6H_5CH_2Br$ | $C_5H_5NBzBr$ [d] | 0.241 | 50 ± 0.5 | 60 ± 5 | 66 ± 1 |
| $CH_3(CH_2)_6CH_2Br$ [e] | None | — | 100 ± 0.5 | No reaction after 8000 min | |
| $CH_3(CH_2)_6CH_2Br$ | $Bu_4NBr$ | 0.109 | 100 ± 0.5 | 80 ± 5 | 70 ± 2 |
| $CH_3(CH_2)_6CH_2Br$ | $Bu_4NBr$ | 0.229 | 100 ± 0.5 | 40 ± 5 | 69 ± 2 |

[a] Determined after about ten reaction half lives. In all cases the presence of unreacted alkyl bromide accounted for the remainder of the material balance. [b] In all runs $[(C_6H_5)_2CHBr] = [Bu_3SnCl] =$ ca. 2.32 *M*. [c] In all runs $[C_6H_5CH_2Br] = [Bu_3SnCl] =$ ca. 2.56 *M*. [d] Generated in situ by the reaction of pyridine with benzyl bromide. [e] In all runs $[CH_3(CH_2)_6CH_2Br] = [Bu_3SnCl] =$ ca. 2.27 *M*.

suggested that the very large rate accelerations produced by added quaternary ammonium bromides in the benzyl and n-octyl bromide reactions can be best explained by a mechanism involving initial coordination of bromide ion with tri-n-butyltin chloride to form a nucleophilic pentavalent tin containing chlorobromotri-n-butyltin anionic complex. This is shown below in simplified form for the forward process:

$$Br^- + Bu_3SnCl \rightleftharpoons Bu_3\overline{Sn}ClBr$$



An analogous scheme can be written for the reverse bromide for chloride substitution on carbon. Support for such a type of mechanism comes, for example from the report [5] that tetraethylammonium bromide and trimethyltin bromide on reaction yield a pentavalent tin-containing dibromotrimethyltin anionic complex.

In the above simplified mechanism, initial coordination of bromide ion with tri-n-butyltin chloride is shown to give a chlorobromotributyltin anion which could serve as the nucleophile for both the forward and reverse processes. However, in the presence of excess tri-n-butyltin chloride and as the reaction progresses to give tri-n-butyltin bromide, several other equilibrium processes, shown below, could come into play [6]. These would produce the additional

$$Bu_3\bar{Sn}ClBr + Bu_3SnCl \rightleftharpoons Bu_3\bar{Sn}Cl_2 + Bu_3SnBr$$

$$Bu_3\bar{Sn}ClBr + Bu_3SnBr \rightleftharpoons Bu_3\bar{Sn}Br_2 + Bu_3SnCl$$

nucleophilic dichlorotributyltin anion and dibromotributyltin anion species. Thus, in reactions using low initial mole ratios of tri-n-butyltin chloride to alkyl bromide and bromide ion catalyst, a complex kinetic behavior would be expected. However, if an initial large excess of tri-n-butyltin chloride over alkyl bromide and bromide ion catalyst is employed, the major nucleophilic species present should be the dichlorotributyltin anion. Its concentration should be equal to the initial bromide ion concentration and remain constant throughout the course of a run. Under such conditions, where also the conversions to products at equilibrium would be high and the nature of the reaction medium would change only slightly over the course of a run, the reactions would be expected to exhibit pseudo-first-order kinetic behavior in alkyl bromide.

To investigate this possibility, we examined the kinetic behavior of the reactions of tri-n-butyltin chloride with benzyl bromide and n-octyl bromide in the presence of catalytic amounts of tetra-n-butylammonium bromide using an initial large ten fold molar excess of tri-n-butyltin chloride over alkyl bromide. As is seen from the data given in Table 2, all of the reactions indeed proceeded essentially to completion, and the kinetic data exhibited good pseudo-first-order rate behavior. Division of the observed pseudo-first-order rate constants by initial tetra-n-butylammonium bromide concentration also gave second-order rate constants which were independent of initial bromide ion concentration within experimental error. Finally, it should be noted that the large, negative

TABLE 2

REACTIONS OF BENZYL BROMIDE AND n-OCTYL BROMIDE WITH TRI-n-BUTYLTIN CHLORIDE, NEAT, IN 1 : 10 MOLAR RATIOS IN THE ABSENCE AND PRESENCE OF ADDED TETRA-n-BUTYLAMMONIUM BROMIDE

| RBr | Additive | [Additive] (*M*) | Temp. (°C) | RCl [a] (%) at equil. | $10^5 k_1$ [b] ($sec^{-1}$) | $10^5 k_2$ [c] ($l\ mol^{-1}\ sec^{-1}$) |
|---|---|---|---|---|---|---|
| $C_6H_5CH_2Br$ [d] | None | — | 100 ± 0.5 | — | 0.083 | — |
| $C_6H_5CH_2Br$ | $Bu_4NBr$ | 0.0211 | 100 ± 0.5 | 97 ± 1 | 62 | 2900 |
| $C_6H_5CH_2Br$ | $Bu_4NBr$ | 0.0362 | 100 ± 0.5 | 96 ± 1 | 110 | 3000 [e] |
| $C_6H_5CH_2Br$ | $Bu_4NBr$ | 0.0348 | 75 ± 0.5 | 98 ± 1 | 12 | 350 |
| $C_6H_5CH_2Br$ | $Bu_4NBr$ | 0.0745 | 75 ± 0.5 | 97 ± 1 | 27 | 360 |
| $CH_3(CH_2)_6CH_2Br$ [f] | None | — | 125 ± 0.5 | — | <0.01 | — |
| $CH_3(CH_2)_6CH_2Br$ | $Bu_4NBr$ | 0.0351 | 125 ± 0.5 | 96 ± 2 | 19 | 540 |
| $CH_3(CH_2)_6CH_2Br$ | $Bu_4NBr$ | 0.0708 | 125 ± 0.5 | 96 ± 2 | 40 | 560 |
| $CH_3(CH_2)_6CH_2Br$ | $Bu_4NBr$ | 0.0359 | 100 ± 0.5 | 97 ± 2 | 3.0 | 84 [g] |
| $CH_3(CH_2)_6CH_2Br$ | $Bu_4NBr$ | 0.0731 | 100 ± 0.5 | 95 ± 2 | 6.0 | 82 |

[a] Determined after about ten reaction half lives. In all cases the presence of unreacted alkyl bromide accounted for the remainder of the material balance. [b] Calculated graphically assuming pseudo-first-order rate behavior. [c] Calculated by dividing the observed pseudo-first-order rate constants by initial $Bu_4NBr$ concentrations. [d] In all runs $[C_6H_5CH_2Br]$ = ca. 0.36 *M* and $[Bu_3SnCl]$ = ca. 3.6 *M*. [e] $\Delta H^{\ddagger} = 21$ kcal/mole, $\Delta S^{\ddagger} = -60$ e.u. [f] In all runs $[CH_3(CH_2)_6CH_2Br]$ = ca. 0.35 *M* and $[Bu_3SnCl]$ = ca. 3.5 *M*. [g] $\Delta H^{\ddagger} = 31$ kcal/mol, $\Delta S^{\ddagger} = -67$ e.u.

−60 and −67 e.u. entropies of activation at 100°C observed for both the benzyl and n-octyl bromide reactions, respectively, are in accord with what would be expected for a bimolecular substitution process involving a nucleophile with large steric requirements.

We next studied briefly whether ligands for trialkyltin halides, such as pyridine and *N,N*-dimethylformamide (DMF), which could potentially form zwitterionic complexes [7] might also exhibit any observable rate accelerating effects in the chloride for bromide redistribution reactions between carbon and tin. Thus, a series of reactions of tri-n-butyltin chloride with n-octyl bromide, neat, in initial 10 : 1 mole ratios were carried out in the presence of initial pyridine and DMF. For comparison, a corresponding reaction was also carried out in the presence of initial 2,6-lutidine. This would be expected to coordinate to only a very small extent, if at all, with the tri-n-butyltin halides.

The data given in Table 3 show that with all three additives the rates of n-octyl chloride formation were faster than in the absence of any additive. However, when the kinetic data were plotted according to a first-order-rate treatment, as was done for the data in the corresponding reactions with added tetra-n-butylammonium bromide, it was found that all were exhibiting upward drifting rate behavior. In the case of the reaction with added initial pyridine this can be explained by the observed formation of *N*-octylpyridinium bromide in the reaction mixture. Thus, it also seems reasonable to attribute the upward drifts in rate for the reactions in the presence of DMF and 2,6-lutidine to some very slow processes which form bromide ion. NMR examination of the reaction mixture did not provide any clearcut evidence for such processes. However, slow formation of 1-octene was observed, and this must be accompanied by hydrogen bromide. Reactions of the hydrogen bromide with DMF and 2,6-lutidine could thus provide the sources of bromide ion.

Unfortunately, all of the upward drifts were too rapid for any meaningful data to be obtained from initial slopes regarding whether or not the free DMF, pyridine, and 2,6-lutidine themselves exert any rate accelerating effects. All

TABLE 3

REACTIONS OF n-OCTYL BROMIDE WITH TRI-n-BUTYLTIN CHLORIDE, NEAT, IN 1 : 10 MOLAR RATIOS [a] IN THE ABSENCE AND PRESENCE OF VARIOUS ADDITIVES AT 125 ± 1°C

| Additive | [Additive] (*M*) | RCl [b] (%) at equil. | Estimated $10^5 k_1$ (sec$^{-1}$) at [c] time for formation of | | |
|---|---|---|---|---|---|
| | | | 5% RCl | 30% RCl | 60% RCl |
| None | — | — | <0.01 [d] | — | — |
| DMF | 0.0715 | >92 | 0.13 | 0.80 | 1.5 [d] |
| 2,6-Lutidine | 0.0633 | >92 | 0.16 | 1.0 | 1.6 [d] |
| Pyridine | 0.0704 | >97 | 3.3 | 10 [e] | 18 [e] |
| $Bu_4NBr$ | 0.0708 | 96 ± 2 | 40 | 40 | 40 |

[a] In all runs [$(CH_3(CH_2)_6CH_2Br$] = ca. 0.35 *M* and [$Bu_3SnCl$] = ca. 3.5 *M*. [b] Determined after about ten reaction half lives. In all cases the presence of small amounts of unreacted alkyl bromide was observed. [c] Estimated graphically from tangents to a plot of log[RBr] versus time. [d] About 10% 1-octene formation was observed. [e] At times for 30% and 60% n-octyl chloride formation the concentrations of *N*-octylpyridinium bromide formed by reaction of n-octyl bromide with pyridine were about 0.022 and 0.036 *M*, respectively.

that can be concluded is that their catalytic effects, if any, must be very much smaller than that produced by bromide ion. This might have been expected since anionic halide ion complexes would definitely be expected to be much stronger nucleophiles than are zwitterionic pyridine or DMF complexes.

## Experimental

### *General comments*

Melting points and boiling points are uncorrected. NMR spectra were run on a Varian Associates A-60A instrument, and chemical shifts are reported in $\delta$(ppm) downfield from tetramethylsilane.

### *Materials*

Benzhydryl bromide; m.p. 43—44°C (lit. [8] m.p. 42°C) was prepared by *N*-bromosuccinimide (NBS) bromination of diphenylmethane and purified by reduced pressure distillation. Benzhydryl chloride, benzyl bromide, benzyl chloride, 1-bromooctane, 1-chlorooctane, 1-octene, tri-n-butyltin chloride, tetra-n-butylammonium bromide, pyridine, 2,6-lutidine and DMF were obtained commercially and if necessary redistilled or recrystallized before use. Tri-n-butyltin bromide, b.p. 108°C/0.5 mmHg, $n_D^{25}$ 1.5010 (lit. [9] b.p. 122°C/1.6 mmHg, $n_D^{25}$ 1.5022) was prepared by the reaction of tri-n-butyltin hydride with ethyl bromide under ultraviolet irradiation.

### *N-Benzyl- and N-1-octylpyridinium bromides*

These were prepared by heating pyridine and a slight excess of the alkyl halide in the absence of a solvent at 100°C. Because the salts were extremely hygroscopic and were already known, they were not isolated and purified but were characterized directly by examination of their NMR spectra. Their NMR absorptions in $CDCl_3$ solution, together with those of pyridine for comparison are as follows; pyridine: $\delta$ 7.2 (t, 2H, *meta* to N), 7.5 (m, 1H, *para* to N) and 8.5 ppm (d, 2H, *ortho* to N); *N*-benzylpyridinium bromide [10]; $\delta$ 6.4 (s, 2H, N—$CH_2$), 7.4 (m, 3H, *meta* and *para* to $CH_2$), 7.8 (m, 2H, *ortho* to $CH_2$), 8.2 (t, 2H, *meta* to N), 8.7 (m, 1H, *para* to N) and 9.8 ppm (d, 2H, *ortho* to N); *N*-1-octylpyridinium bromide [11]; $\delta$ 0.9—2.2 (m(br), 15H, $CH_3(CH_2)_5CH_2$), 5.1 (t, 2H, N—$CH_2$), 8.3 (t, 2H, *meta* to N), 8.8 (m, 1H, *para* to N) and 9.8 ppm (d, 2H, *ortho* to N).

### *Reaction studies*

All reactions were run on millimole scale in small, sealed ampoules or in NMR tubes. Both the rates of disappearance of the starting alkyl bromides and the rates of appearance of the product alkyl chlorides were followed. The products of the reactions were identified by comparison with authentic samples. The reactions of n-octyl bromide were analyzed directly without prior workup by GLPC using an SE 30 column and/or using quantitative NMR techniques in comparison with spectra of known mixtures of n-octyl bromide and n-octyl chloride dissolved in tri-n-butyltin chloride. The agreement in the results from the two analytical methods was checked and found to be excellent. The other reactions were followed only using NMR techniques by direct examination of the reaction mixtures without any prior workup. The chemical shift values of the absorptions used during NMR analysis of the various reaction mixtures were: benzhydryl bromide ($\delta$ 6.2, s, CHBr), benzhydryl chloride ($\delta$ 6.1, s, CHCl), benzyl bromide ($\delta$ 4.3, s, $CH_2Br$), benzyl chloride ($\delta$ 4.4, s, $CH_2Cl$), n-octyl bromide ($\delta$ 3.4, t, $CH_2Br$), n-octyl chloride ($\delta$ 3.6, t, $CH_2Cl$), 1-octene ($\delta$ 5.1, t(br), $=CH_2$) and 5.3, m(br), CH=), tetra-n-butylammonium bromide ($\delta$ 3.1, m(br), CH—N), *N*-benzylpyridinium bromide ($\delta$ 5.8, s, $NCH_2$) and ($\delta$ 8.9, d, *ortho* to N), DMF ($\delta$ 2.8 and 3.0, d, $(CH_3)_2N$) and ($\delta$ 7.8, s, HC=O), 2,6-lutidine ($\delta$ 2.4, s, $CH_3$), pyridine ($\delta$ 7.7, m, *para* to N) and 8.4, d, *ortho* to N), and *N*-octylpyridinium bromide ($\delta$ 8.6, d, *ortho* to N). Note that these values varied slightly in different reaction mixtures and with differing initial mole ratios of tri-n-butyltin chloride to alkyl bromide. Thus, they should only be taken as indicative of the general absorption patterns.

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