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COMMUNICATION

The direct synthesis of triorgano tin compounds

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The synthesis of triorganotin halides directly from tin is described. The addition of an alkyl halide to tin metal dispersed in a molten quaternary halide rapidly and selectively produces the trialkyltin halide and a by-product containing the quaternary as a tin halide complex. The quaternary halide, the tin, and the halide ion are all recovered from the by-product by electrolysis and reused.

Keywords: Triorgan halides, synthesis, electrolysis, tin metal

INTRODUCTION

Organotin compounds are very widely used industrial chemicals; Smith,[1] and Bennett[2] have produced fairly recent reviews. The two major uses are the diorganotins (R_2SnX_2) employed in PVC stabilisation and the triorganotins (R_3SnX) used in biocides.

Both of these types of organotin compound are commonly made by indirect processes via the tetrasubstituted compounds which in turn are made indirectly using the aluminium alkyl or Grignard routes (see Gmelin[3]). These can be described by Eqns [1], [2], and [3].

$$4R_2Al + 3SnCl_4 + 4R'_2O \rightarrow 3R_4Sn + 4AlCl_3.R'_2O \quad [1]$$

$$3R_4Sn + SnCl_4 \rightarrow 4R_3SnCl \quad [2]$$

$$R_4Sn + SnCl_4 \rightarrow 2R_2SnCl_2. \quad [3]$$

The diorganotin dihalides may also be synthesised directly from tin as in Eqn [4]

$$2RX + Sn \rightarrow R_2SnX_2. \quad [4]$$

The direct process has been reviewed by Murphy and Poller[4] and by Kizlink[5] and is of limited industrial use since the dominant product is the diorganotin. Bennett[2] states that the direct process cannot yield trialkyltin compounds.

Other routes to triorganotin compounds

Attempts have been made (see Gmelin[3]) to synthesise the triorganotin halides by a more direct route than that involving the tetraorganotin compound; these have usually involved another metal, as in Eqn [5]

$$3RX + Sn + M \rightarrow R_3SnX + MX_2 \quad [5]$$

(where M = Zn, Mg; Na may also be used)

Such processes have not been used commercially because they are difficult to control and the metal and halogen are lost.

A means of improving this would be to recover the metal and halogen by electrolysis (see Eqn [6]).

$$MX_2 \rightarrow M + X_2. \quad [6]$$

However in aqueous systems the recovery of sodium and magnesium is impossible, but zinc can be electrodeposited from an aqueous electrolyte so a zinc based route might be economically feasible. A further extension would be to use tin to alkylate itself, as in Eqn [7], with the electrolytic recovery of the tin now an

$$3RX + 2Sn \rightarrow R_3SnX + SnX_2 \quad [7]$$

important requirement because tin is very expensive (about £4000 per tonne; Nov 1986). Sisido[6] demonstrated that the direct reaction of tin with benzylchloride in the presence of water gave high yields of tribenzyltin chloride, Eqn [8]

$$3\,C_6H_5CH_2Cl + 2Sn \xrightarrow{H_2O} (C_6H_5CH_2)_3SnCl + SnCl_2 \qquad [8]$$

but he was unable[7] to make the process work as efficiently with the much less active alkyl halides, producing mixtures of R_2SnX_2 and R_3SnX. However Sisido[8] was able to further butylate di-*n*-butyltin dichloride using an organic base, tin, and butyl chloride.

EXPERIMENTAL

The direct synthesis of triorganotin compounds

In examining these areas of chemistry in a search for a direct route to triorganotin compounds the following targets were set:

(a) There should be a direct route from tin metal, with any other metal being present only in small or catalytic quantities
(b) the by-product tin would be recovered electrolytically
(c) the halogen would also be recovered so that the more expensive alkyl bromide or iodide might be used.

The direct routes [3], [4], [5] to the diorganotins were examined, and in particular the catalysts; these are typically quaternary halide or trialkyl derivative of Group V elements, R_4QX or R_3Q (Q = N, P or Sb) or better, as preformed tin halide complexes. A typical process for the dialkyltins involves dissolving the catalyst in excess of the alkyl halide, adding tin (as granules or powder) and heating until the tin dissolves. This is followed by by distillation to recover the excess alkyl halide and the diorganotin dihalide, leaving the quaternary compound as a tin halide complex which can be reused as the catalyst. Such processes can produce pure diorganotin dihalides with very little triorganotin halide, although mixtures of triorgano- and diorganotins have also been reported.[8,9]

It was discovered that using a quaternary Group V halide as a reagent rather than a catalyst and as a melt rather than in solution, and adding alkyl halide to this melt in the presence of tin we could produce the triorganotin halide very efficiently. The overall process can be described by Eqn [9],

$$3\,RX + R'_4QX + 2\,Sn \rightarrow R_3SnX + R'_4QSnX_3 \quad (Q = N, P, As, Sb) \qquad [9]$$

but it is more complicated than this implies.[10]

The quaternary compound, in functioning as a solvent, permits the attainment of relatively high reaction temperatures (120–140°C). Thus the reaction is conveniently run by adding the alkyl halide to the melt containing a slight excess of tin so that the alkyl halide is consumed more or less as it is added. The quaternary compound used was normally Bu_4NBr but various other Group V onium compounds are also successful. Ternary alkyl compounds of sulphur or selenium can also be used. By using mixtures of alkyl halides mixed organotin products may be produced.

The process is rapid, selective, and very efficient, producing 95%+ yields of R_3SnX (for example, R = butyl, X = Br) containing only 1–2% R_2SnX_2. However half of the tin used, the quaternary reagent, and the halogen from the three alkyl halides are all present in the by-product (R'_4QSnX_3) and clearly must be recovered to make such a process economic. The organotin product, R_3SnX, and the by-product, R'_4QSnX_3, can be separated by conventional means such as solvent extraction or distillation.[10]

The electrolytic recovery of the reagents

The by-product, R'_4QSnX_3, is a salt which melts at low temperatures (about 100°C) but is a poor electrolytic conductor. However in examining its electrochemical properties it was realised that the cathodic deposition of tin (as part of the tin recovery) would require the transfer of halide ion into an aqueous system so that the halide could also be recovered. This led to a two phase electrolysis system in which tin and R'_4QX are recovered in the cathodic nonaqueous phase (which is composed of the by-product) and halide is recovered in the anodic aqueous phase.[11] The electrolysis uses a membrane cell[11] and is described by Eqn [10]

$$2\,NaOH + R'_4QSnX_3 \xrightarrow{+2\ \text{Faradays}} 2\,NaX + R'_4QX + Sn + \tfrac{1}{2}O_2 + H_2O \qquad [10]$$

This electrolysis produces:

(a) R'_4QX and tin which can be reused in the R_3SnX-forming reaction Eqn [9].

(b) Aqueous NaX solution which can be reacted with an alcohol to produce the alkyl halide.[12]

The overall process to commercial triorganotin compounds

Bis-tributyltin oxide [$(Bu_3Sn)_2O$ also known as TBTO] is the basic biocidal ingredient in the more modern and efficient antifouling paints and wood preservatives. It is commonly prepared by hydrolysing tributyltin chloride prepared according to Eqns [1] and [2]. It can now be prepared by combining Eqn [9] (R = butyl, X = Br) and the electrolysis, Eqn [10] (X = Br). Since the bromide can be recovered as butyl bromide[12] this gives an overall process to TBTO using the commodity chemicals *n*-butanol, sulphuric acid, sodium hydroxide, and tin metal. Further experimental details of the preparations and electrolysis will be published shortly.[13]

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REFERENCES

1. Smith, P J and Smith, L *Chem. Br.*, 1975, 11: 208
2. Bennett, R F *Ind. Chem. Bull.*, 1983, 171
3. *Gmelin Handbuch der Anorganischen Chemie, Sn, Organotin Compounds*, Parts 5, 6, and 7, Springer Verlag, Berlin, 1978, 1979, 1980
4. Murphy, J and Poller, R C *J. Organomet. Chem. Lib.*, 1979, 9: 189
5. Kizlink, J *Chem. Listy*, 1984, 78: 134
6. Sisido, K. Takeda, Y and Kinugawa, Z *J. Am. Chem. Soc.*, 1961, 83: 538
7. Sisido, K, Kozima, S. and Tuzi, T *J. Organomet. Chem.*, 1967, 9: 109
8. Sisido, K and Kozeima, S *J. Organomet. Chem.*, 1968, 11: 503
9. Matschiner, H, Voigtlander, R and Tzschach, A *J. Organomet. Chem.*, 1974, 70: 387
10. US Patent 4,510,095 (1985); *Applied Organometallic Chemistry*, (to be submitted for publication)
11. US Patent 4,437,949 (1984)
12. Gilman, H and Blatt, A H (eds), *Org. Synth.*, Collective volume 1, 29, John Wiley and Sons, New York, 1948
13. *Applied Organometallic Chemistry* (to be submitted for publication)