NOTES

THE SMALL-SCALE SYNTHESIS OF ^{13}C-LABELLED METHYLTIN IODIDES

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In connection with other studies, we have synthesised methyltin triiodide and trimethyltin iodide enriched with ^{13}C in the methyl groups. The methods of equations (1)-(4) and (5) were adequate, and the most satisfactory procedures were as described below.

$$\mathrm{SnCl_2 + 4KOH \longrightarrow [K_2SnO_2] + 2KCl + 2H_2O} \tag{1}$$

$$\mathrm{[K_2SnO_2] + {}^{13}CH_3I \longrightarrow [{}^{13}CH_3SnO.O^{-}K^{+}] + KI} \tag{2}$$

$$\mathrm{2\,[{}^{13}CH_3SnO.O^{-}K^{+}] + CO_2 \longrightarrow 2[{}^{13}CH_3SnO.OH] + K_2CO_3} \tag{3}$$

$$\mathrm{[{}^{13}CH_3SnO.OH] + 3HI \longrightarrow {}^{13}CH_3SnI_3 + 2H_2O} \tag{4}$$

$$\mathrm{{}^{13}CH_3SnI_3 + 2(CH_3)_4Sn \longrightarrow {}^{13}CH_3(CH_3)_2SnI + 2(CH_3)_3SnI} \tag{5}$$

METHYLTIN TRIIODIDE

A solution of potassium hydroxide (3.3g.; 58.9 mmol) in water (13 ml.) was cooled to 0°C and slowly added to a stirred solution of stannous chloride (1.40 g.; 7.38 mmol.) in water (3.0 ml.) maintained at 0°C. The resulting solution was filtered and maintained at 0°C. Methyl iodide (1.00 g.; 7.04 mmol.; enriched 60% with ^{13}C) was dissolved in absolute ethanol (3.0 ml.), cooled to 0°C, and then added to the potassium stannite solution with the aid of more alcohol (3 x 1.0 ml.). The flask was stoppered and the mixture stirred magnetically at 0°C for one hour, during which time the methyl iodide slowly dissolved. Stirring was continued for one further hour at 0°C, and then overnight (ca. 13 hours) at room temperature. The solution was then cooled to and maintained at 0°C by the addition of small pieces of solid carbon dioxide, and gaseous carbon dioxide passed through for 2 hours. A white finely crystalline precipitate was produced. The volatile components were removed under reduced pressure (rotary evaporator; pressure ca. 20 mm. Hg; temperature $\leqslant$ 50°), leaving a white solid mass. Water (10 ml.) and carbon tetrachloride (10 ml.) were added, and concentrated hydriodic acid added to the stirred mixture until no solid remained. The organic layer was separated, and the aqueous layer extracted further with carbon tetrachloride (5 x 10 ml.). The six extracts were successively washed with the same sample of water (10 ml.) and dried with the same sample of anhydrous sodium sulphate. The carbon tetrachloride was removed from the combined extracts under reduced pressure (rotary evaporator) and the resulting yellow solid recrystallised from light petroleum (b.p. 40-60°C) to give pure methyltin triiodide. The two aqueous layers were combined, evaporated to a smaller volume (rotary evaporator) and the extraction process repeated. Iteration of the evaporation, extraction and recrystallisation procedure, followed by a final extraction of the ultimately produced solid residue, together with appropriate recycling of mother liquors, gave a total yield of 2.54g. (4.94 mmol.; 70.2% based on $^{13}CH_3I$) of the recrystallised methyltin triiodide, and a further 0.62 g. of crude product by evaporation of the final mother liquor, giving a total recovered yield of 3.16 g. (6.14 mmol.; 87.3%). Transfer of isotopic purity was quantitative (integrated proton NMR spectrum).

TRIMETHYLTIN IODIDE

Methyltin iodide (1.00 g.; 1.94 mmol.; enriched 60% with ^{13}C; prepared as above) and tetramethyltin (0.70 g.; 3.91 mmol.) were mixed in a 5 ml. flask and heated under dry nitrogen in a bath at 180°C until refluxing ceased (*ca.* 4.5 hours) and then for a further 3 hours. Distillation with the receiving vessel cooled to 0°C yielded a small amount of tetramethyltin (b.p. *ca* 75°) and then pure trimethyltin iodide as a clear very pale yellow liquid, b.p. 170 ± 10°C (1.42g.; 4.88 mmol.; 84% based on methyltin triiodide). The integrated proton NMR spectrum showed that this was enriched to *ca.* 8% with ^{13}C.

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