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THE FORMATION OF TRI-n-BUTYLTIN FLUORIDE FROM TETRAFLUOROHYDROQUINONE

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SUMMARY

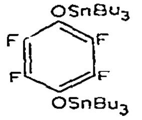
Reaction of tetrafluorohydroquinone with tri-n-butyltin chloride or bis(tri-n-butyltin) oxide has been found to produce tri-n-butyltin fluoride.

INTRODUCTION

The conventional preparation of organotin fluorides is from silver fluoride and the appropriate organotin chloride[1]. It has previously been shown in these laboratories that heating solid ammonium fluoride with bis(tri-n-butyltin) oxide or tri-n-butyltin chloride leads to the quantitative formation of tri-n-butyltin fluoride[2]. Recently we have refined this technique by dissolving bis(tri-n-butyltin) oxide in toluene and adding an aqueous solution of ammonium fluoride whilst stirring vigorously at room temperature, a method analogous to the interfacial condensation procedure for the preparation of organotin esters[3]. The insoluble tri-n-butyltin fluoride is simply filtered off and recrystallised from methanol in the usual way.

RESULTS AND DISCUSSION

In the course of work involving derivatives of fluorinated phenols, a hexane solution of tri-n-butyltin chloride was added at room temperature and under a nitrogen atmosphere, to a vigorously stirred aqueous solution of tetrafluorohydroquinone neutralized with sodium hydroxide with the intention of obtaining compound (I) below. Evaporation of the hexane layer, after a 5 h reaction period, gave a dark brown oil which deposited crystals of tri-n-butyltin fluoride, identified by its melting point, IR spectrum and elemental analysis.



(I)

Tri-n-butyltin fluoride was also isolated from the organic layer together with an unidentified dark brown oil, after a hexane solution of tri-n-butyltin chloride was stirred at room temperature for 48 h with an aqueous solution of tetrafluorohydroquinone.

When tetrafluorohydroquinone and bis(tri-n-butyltin) oxide were heated together at 130° in the absence of solvent a dark brown residue and tri-n-butyltin fluoride were again produced.

Several additional points are of interest. Firstly, pentafluorophenol reacted readily with tri-n-butyltin chloride by the interfacial method to give tri-n-butyltin pentafluorophenate[4] and secondly, reaction under the same conditions of a hexane solution of tri-n-butyltin chloride with an aqueous neutralized solution of hydroquinone produced only a dark brown residue. Thirdly an aqueous solution of tetrafluorohydroquinone, containing an excess of NaOH, when shaken in air and reacidified with dilute HCl gave a negative test for fluoride ion with zirconium–alizarin reagent[5]. A similar basic solution of tetrafluorohydroquinone when shaken with a hexane solution of tri-n-butyltin chloride and the aqueous layer reacidified, gave a positive fluoride test.

EXPERIMENTAL

The reaction of tri-n-butyltin chloride with neutralized tetrafluorohydroquinone is typical of the procedure employed.

Sodium hydroxide (0.5 g, 0.0125 mole) in water (50 ml) was added to tetrafluorohydroquinone (1.0 g, 0.0054 mole) in water (100 ml) at 18°, under a nitrogen atmosphere. Tri-n-butyltin chloride (3.5 g, 0.0107 mole) in n-hexane (150 ml) was added to the light pink solution and the mixture was stirred for 5 h at 18°. The organic layer was then separated and washed with water until the washings did not give a positive chloride test with silver nitrate solution. The combined aqueous layers were acidified with dilute HCl, extracted with ether (2 × 150 ml), the extracts combined dried ($MgSO_4$) and the ether distilled to leave a trace of a dark brown oil. The dark red hexane layer was distilled on a steam bath to leave a dark brown oil which deposited white crystals on standing. These were recrystallised from methanol as white crystals of tri-n-butyltin fluoride (0.25 g, 0.00080 mole, 7.5% yield) with correct m.p. and IR spectrum. (Found: C, 46.3; H, 8.6. $C_{12}H_{27}FSn$ calcd.: C, 46.6; H, 8.7%.)

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