Synthesis & Reactions of Some Phenylcyclopentadienyltin Compounds

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Cyclopentadienylthallium (CpTl) reacts with Ph2SnCl2 and Ph3SnI to yield Ph2SnCpCl and Ph3SnCp respectively. Ph3SnCp reacts with I2 to afford Ph3SnI, indicating preferential cleavage of Cp-Sn bond by I2 over the Ph-Sn bond.

The cleavage reactions of tetraorganotins have been studied in detail. However such studies on diorganotins and triorganotins have not so far been reported. We wish to report the cleavage reactions of Ph2SnCl2 and Ph3SnI with CpTl and of Ph3SnCp with I2. These cleavage reactions provide convenient synthetic routes to phenylcyclopentadienyltin compounds and indicate preferential cleavage of Cp-Sn bond in comparison to Ph-Sn bond.

Ph2SnCl2 and Ph3SnI were prepared in the laboratory and iodine (Rhodia, BP grade) was sublimed before use.

Desired amount of fresh monomer cyclopentadiene, obtained by cracking the commercially available sample (dimer), was directly distilled into an aqueous solution of thallous sulphate (BDH) containing a little methanol. It resulted in the immediate precipitation of CpTl which was washed with water and methanol and dried at 20°/10 mm Hg.

All the reactions and their work-up were carried out under N2 atmosphere and physicochemical measurements were done as before.

Cleavage of Ph2SnCl2 with CpTl (1:1)

To a solution of Ph2SnCl2 (3.44 g, 0.01 mol) in anhydrous chloroform (25 ml) was added a suspension of CpTl (2.69 g, 0.01 mol) in the same solvent (30 ml) and the mixture stirred for 5 hr at room temperature. Precipitated TICl (2.16 g, 90.3%) was filtered off, and the filtrate concentrated to ~10 ml. Addition of ether (~8 ml) precipitated a solid, which was washed with ether, dried at 20°/10 mm Hg and identified as Ph2SnCpCl (1.93 g; 51.7%), m.p. >240° (lit.3 b.p. 120°/8.10^{-4} mm) [Found: Sn, 31.79; C, 54.52; H, 3.98; Cl, 9.48 C17H16ClSn requires Sn, 31.86; C, 54.61; H, 4.02; Cl, 9.50%]; IR (KBr): 3025 (Cp stretch), 805 cm^{-1} (Cp bend).

Cleavage of Ph3SnI with CpTl (1:1)

To a solution of CpTl (2.69 g, 0.01 mol) in anhydrous chloroform (25 ml) was added a solution of Ph3SnI (4.77 g, 0.01 mol) in chloroform (30 ml) dropwise at room temperature. The mixture was stirred for 2 hr, the precipitated greenish yellow TII (3.14 g, 94.8%) filtered off and the solution concentrated (~3 ml). To the residual matter was added pet. ether (60-80°) and dried at 20°/10 mm Hg; yield 2.49 g (60%), m.p. 129°-4 (lit.5 m.p. 130-31°).

Cleavage of Ph3SnCp with I2 (1:1)

To a solution of Ph3SnCp (4.15 g, 0.01 mol) in CCl4 (20 ml) was added a solution of I2 (2.54 g, 0.01 mol) in the same solvent (30 ml), slowly dropwise at 0°C with constant stirring. The reaction mixture was further stirred for 2 hr and the precipitated AgCl and excess silver acetate were filtered off. The filtrate was concentrated (~4 ml) and to the concentrate was added pet ether (60-80°) to give Ph3SnAc as a brown solid which was washed with pet ether (60-80°) and dried at 20°/10 mm Hg (Found: Sn, 29.95, C, 57.26; H, 4.49; C17H18O2Sn requires Sn, 29.97; C, 57.43; H, 4.53%; yield 1.78 g (45%); m.p. >240°; IR(KBr): 3020 (Cp stretch), 1560 (vC=O), 1430 (vC=O), 800 cm^{-1} (Cp bend).

CpTl selectively removes one Cl from Ph2SnCl2 to form Ph2SnCpCl and thallous chloride. Similarly CpTl, when reacted with Ph3SnI, removes an iodine atom to form Ph3SnCp and thallous iodide. Those cleavage reactions provide convenient synthetic routes for the preparation of phenylcyclopentadienyltin compounds3-5. On treating Ph3SnCp with I2, Ph3SnI is obtained, indicating preferential cleavage of Sn-Cp bond by I2 as compared to Sn-Ph bond.

IR data (ΔνCOO = νas COO - νs COO = 130 cm^{-1}) suggest Ph3SnCpAc to be polymeric in the solid state with bridging acetate groups and ester-like in dilute solution6 (the molar conductance of 10^{-3} M solution in nitrobenzene is 4.60 ohm^{-1} cm^{2} mol^{-1} and observed molecular weight is 368 in the same solvent as against the calculated value of 397).
In 90 MHz PMR spectra, the lower field multiplet and the high field multiplet corresponding to \( \alpha \)-protons and \( m \)- and \( p \)-protons of phenyl groups attached to Sn appear at \( \delta \) 7.90, 7.20, 7.54, 7.14 and 7.56, 7.32 for \( \text{Ph}_2\text{SnCpCl}, \text{Ph}_2\text{SnCpAc} \) and \( \text{Ph}_3\text{SnCp} \) in DMSO-\( d_6 \), CDCl\(_3 \) and CDCl\(_3 + \text{DMSO-}d_6 \) respectively. The methyl protons in \( \text{Ph}_2\text{SnCpAc} \) appear as a singlet at \( \delta \) 1.95. The presence of singlets at \( \delta \) 6.19, 6.73 and 6.97 in \( \text{Ph}_2\text{SnCpCl}, \text{Ph}_2\text{SnCpAc} \) and \( \text{Ph}_3\text{SnCp} \) respectively indicates occurrence of a fast degenerate metallotropic rearrangement over the cyclopentadienyl ring by 1,2- shift mechanism.

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References