Diorganochlorotin Perfluorocarboxylates

By CHARLENE SHIOW-CHYN WANG and JEAN'NE M. SHREEVE*
(*Department of Chemistry, University of Idaho, Moscow, Idaho* 83843)

Summary Triorganotin chlorides are easily converted into diorganochlorotin perfluorocarboxylates, accompanied by the formation of the appropriate alkane or benzene, by perfluorocarboxylic acids.

DIALKYLCHLOROTIN CARBOXYLATES (R_2SnClO_2CR) have been prepared by various methods including the reactions of dialkyltin dichlorides with carboxylic acids or salts of these acids.[1] We report the synthesis of organochlorotin perfluorocarboxylates in high yield *via* the reactions of triorganotin chlorides with perfluorocarboxylic acids,

$$R^2_3SnCl + R^1CO_2H \rightarrow R^1CO_2SnClR^2_2 + R^2H$$

$$R^1 = Me, CF_3, C_2F_5, C_3F_7, CF_2Cl$$

$$R^2 = Me, Ph, Bu$$

Only the dimethylchlorotin acetate was previously known.[1]

We are prompted by the observations of Aubke *et al.*,[2] on the reactions of HSO_3R (R = F, CF_3, Cl, Me, Et) with trimethyltin chloride to yield both HCl and methane, to report our results. These workers suggest the initial replacement of chloride by the acid anion followed by the production of methane. The intermediate trimethyl compound was not reported.

While we find the reactions of triphenyltin chloride with the acids occur readily at room temperature and are exothermic, formation of the dialkylchlorotin perfluorocarboxylates requires heating the reactants at 100° for a few hours. Benzene or alkane is quantitatively produced when the acid : tin compound ratio is equal to or greater than one. Heating at 100° in the presence of a large excess of acid does not alter the yield of one mole of benzene or alkane per mole of tin compound used. The excess of acid may be distilled away under vacuum to leave white, crystalline, water-insensitive solids which are insoluble in nonco-ordinating solvents and water. They dissolve in dilute acidic solution, and chloride ion can be determined quantitatively.

I.r. spectra show the existence of the Sn–Cl bond stretching frequency in the range 330—318 cm^{-1}. Since both asymmetric and symmetric Sn–C stretching frequencies are observed at about 380 and 520 cm^{-1}, respectively, the C–Sn–C angle must be less than 180°. It is likely that these solids are polymeric chains consisting of five-co-ordinated tin atoms with bridging perfluorocarboxylate groups as suggested for Me_2SnClO_2CMe[3] and $R^1_3SnO_2CR^2$.[4] Mössbauer spectral studies are under way.

These diorganochlorotin perfluorocarboxylates form 1 : 1 addition compounds with amines and pyridine at room temperature without solvent. All new compounds have been characterized *via* mass and i.r. spectra as well as elemental analyses.

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