

A NOVEL PURIFICATION OF NONVOLATILE ORGANOTIN HALIDES

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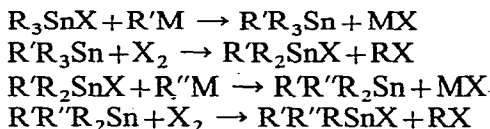
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SUMMARY

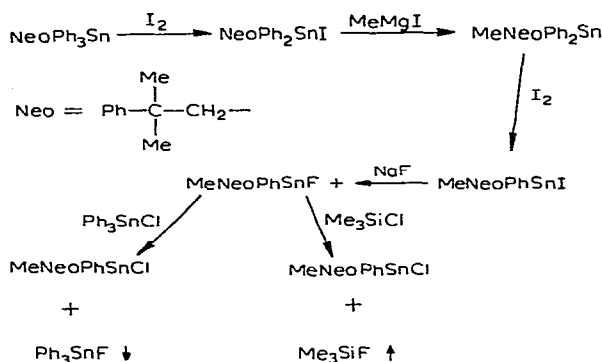
Crude noncrystallisable methylneophylphenyltin iodide, prepared in several steps without purifying the intermediates, was converted to the corresponding sparingly soluble fluoride. This latter was purified by recrystallization from methanol and was converted into pure methylneophylphenyltin chloride by quantitative halide-halide exchange with trimethylchlorosilane or triphenyltin chloride.

Asymmetrically substituted organotin halides are commonly prepared from the commercially available trimethyltin chloride or triphenyltin chloride by the sequence of reactions shown below¹⁻⁴:



A variety of conditions have been used for the cleavage reaction with the greatest selectivity being reported for systems employing methanol as a solvent^{3,4}. When comparatively low molecular weight products such as methylethylphenyltin chloride are prepared, they are readily purified by distillation under reduced pressure. However, higher molecular weight products are often too involatile to distil and are apparently of too low a symmetry to crystallize.

In connection with a study of asymmetric organotin compounds^{5,6} we have devised a novel procedure for purifying nonvolatile organotin halides via the insoluble tin fluoride. To demonstrate the usefulness of this method we prepared a crude sample of methylneophylphenyltin iodide (I) from neophyltriphenyltin without isolation of the intermediate products. Treatment with aqueous sodium fluoride gave methylneophylphenyltin fluoride which was readily purified by recrystallization from methanol. The fluoride was then converted to the analogous chloride, (III), by halide-halide exchange employing either triphenyltin chloride which leads to precipitation of the more insoluble triphenyltin fluoride or trimethylchlorosilane which leads to the loss of the volatile trimethylfluorosilane.



EXPERIMENTAL

Neophyltriphenyltin

The Grignard reagent prepared from 86 g (0.51 mole) of neophyl chloride and 13.5 g (0.55 g-atom) of magnesium in 400 ml of ethyl ether was slowly added to 175 g (0.46 mole) of triphenyltin chloride in 250 ml of toluene. The ether was distilled off until the temperature reached 100° and then the reaction mixture was refluxed for 3 h. The reaction mixture was then added to dilute hydrochloric acid, washed with water and dried over sodium sulfate. Following removal of the solvent under reduced pressure, the residue was recrystallized from ethanol/benzene mixtures to obtain 215 g (97%) of neophyltriphenyltin, m.p. 93–95°. (Found: C, 69.7; H, 5.99. $\text{C}_{28}\text{H}_{28}\text{Sn}$ calcd.: C, 69.6; H, 5.84%.)

Methylneophylphenyltin fluoride

A solution of 10.2 g (0.041 mole) of iodine in 200 ml of ethyl ether was slowly added to a vigorously stirred solution of 20 g (0.041 mole) of neophyltriphenyltin in 200 ml of carbon tetrachloride. Following the disappearance of the iodine color the volatile solvents were removed under reduced pressure. The resultant mixture of crude neophyldiphenyltin iodide and iodobenzene was dissolved in 300 ml of ethyl ether and 80 ml (0.08 mole) of a 1.0 *M* ethereal solution of methylmagnesium iodide was added. The reaction mixture was stirred for 15 min and then added to dilute hydrochloric acid and ice. The ethereal layer was washed with water, dried over magnesium sulfate and then concentrated under reduced pressure. The resultant crude methylneophyldiphenyltin was dissolved in 300 ml of ethyl ether and titrated with a 0.2 *M* ethereal solution of iodine. The progress of the cleavage reaction was monitored by the disappearance of the methyl peak of the methylneophyldiphenyltin and the simultaneous appearance of a peak for the methyl group of methylneophylphenyltin iodide in the NMR spectrum of the reaction mixture. The end point was reached when 155 ml (0.031 mole) of iodine solution had been added. The reaction mixture was concentrated under reduced pressure (100°/0.01 mm) to obtain 7.9 g (41%) of crude methylneophylphenyltin iodide.

When 1.0 g of sodium fluoride in 25 ml of water was added to a boiling solution of 6.0 g of the crude iodide in 130 ml of 80% aqueous ethanol a white precipitate formed. After standing overnight at room temperature the solution was concentrated under reduced pressure to approximately 30 ml volume. The white solid was separated

by filtration and washed with ether. The 4.4 g of methylneophylphenyltin fluoride, m.p. 148°, was recrystallized twice from methanol to obtain an analytical sample, m.p. 152.5°, (Found: C, 56.4; H, 5.98; Sn, 32.7. $C_{17}H_{21}FSn$ calcd.: C, 56.2; H, 5.84; Sn, 32.7%.)

Methylneophylphenyltin chloride

A. A mixture of 1.89 g (0.0049 mole) of triphenyltin chloride and 1.79 g (0.0049 mole) of methylneophylphenyltin fluoride in 20 ml of ethyl ether was refluxed for 4 h and then stirred for 20 h at room temperature. The solid was filtered off and identified as triphenyltin fluoride by mixed m.p. with an authentic sample. The filtrate was concentrated under reduced pressure and finally kept at 80°/0.05 mm for 2 h. The resultant 1.65 g (88%) of clear, viscous liquid was methylneophylphenyltin chloride. (Found: C, 54.4; H, 5.63; Sn, 30.6; Cl, 9.22. $C_{17}H_{21}ClSn$ calcd.: C, 53.8; H, 5.48; Sn, 31.3; Cl, 9.34 %.)

B. A solution of 0.5 g (0.0014 mole) of methylneophylphenyltin fluoride and 2 ml (0.016 mole) of trimethylchlorosilane in 10 ml of benzene was stirred at room temperature for 4 h. The volatile material was removed under reduced pressure and finally kept at 0.001 mm for 6 h to obtain 5.2 g (99%) of methylneophylphenyltin chloride. (Found: C, 53.9; H, 5.42. $C_{17}H_{21}ClSn$ calcd.: C, 53.8; H, 5.58%.)

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