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Preliminary communication

Some reactions of organotin compounds under γ-irradiation

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SUMMARY

Reaction of organotin compounds with pentafluorobenzene under the influence of γ-radiation produces organotin fluorides.

Ultraviolet radiation is known to cause stepwise degradation of organotin compounds[1], ultimately to metallic tin, but little has been published about the effects of γ-radiation on these compounds. We now report the preliminary results of some γ-radiation induced reactions between organotin compounds and pentafluorobenzene. The objective of this work was to investigate the preparation of fluoroaromatic-substituted organotin compounds by this technique.

The γ-irradiation of solutions of organotin compounds in hexane or benzene produced trace amounts of the stepwise degradation products, which were detected in the reaction mixture by thin-layer chromatography. Thus tetrabutyltin gave trace amounts of tributyltin and dibutyltin compounds and similarly tributyltin chloride gave traces of tetrabutyltin and a dibutyltin compound. The same treatment applied to dibutyltin dichloride produced traces of tetrabutyltin and a tributyltin compound in the resulting solution and a deposit of crystals of stannous chloride (6.6% based on original amount of organotin). Butyltin trichloride gave a tarry residue on irradiation in hexane while bis(tri-n-butyltin) oxide yielded a precipirate of dibutyltin oxide (16.4%).

γ-Irradiation of tetrabutyltin in pentafluorobenzene resulted in a copious precipitate of tributyltin fluoride. After irradiation of a hexane solution containing approximately equimolar amounts of tetrabutyltin and pentafluorobenzene a small amount of insoluble dibutyltin difluoride (0.1%) was separated from the now viscous hexane solution which gave a precipitate of tributyltin fluoride (7.8%) on dilution with acetone. We have previously shown that tributyltin fluoride produces viscous solutions in hexane[2].

Similarly irradiation of hexabutylditin in pentafluorobenzene yielded small amounts of dibutyltin oxide (4.1%) from trace impurities such as water or oxygen and tributyltin fluoride (10.6%). A hexane solution of tributyltin chloride and pentafluorobenzene gave only a precipitate of dibutyltin difluoride (5.8%) with no evidence of tributyltin fluoride whilst dibutyltin dichloride and pentafluorobenzene in hexane produced a precipitate of stannous chloride (3.0%) and no tributyltin fluoride or dibutyltin difluoride. An intractable tarry residue resulted from the irradiation of a hexane solution containing butyltin trichloride and pentafluorobenzene but a similar solution containing bis(tributyltin) oxide and pentafluorobenzene gave only a precipitate of dibutyltin oxide (21.2%).

When tetrabutyltin and perfluoro(dimethylcyclohexane) in hexane were irradiated a precipitate of dibutyltin difluoride (0.4%) in a viscous solution of tributyltin fluoride (3.6%) was obtained. This suggests that fluorine abstraction under irradiation can occur with alicyclic as well as with aromatic fluorine compounds.

EXPERIMENTAL

The irradiations were conducted in Quickfit stoppered glass test tubes under an atmosphere of nitrogen with the reactants (3 mmol of each) dissolved in hexane (5 ml). The radiation was supplied by a 1500 Curie cobalt-60 source built to the design of the Australian Atomic Energy Commission giving a dose rate of 1.5 $kJ \cdot kg^{-1} \cdot h^{-1}$, as measured by ferrous sulphate dosimetry. The tubes received a dose in the range 220—285 $kJ \cdot kg^{-1}$. The temperature of the samples during the irradiation was about 30°. Thin-layer chromatography was used to examine all the irradiated solutions using well documented methods to differentiate between mono- di-, tri- and tetraalkyltin compounds[3]. This technique does not identify the anion present in the solution.

After irradiation all the solutions were centrifuged to remove any precipitate present. Acetone (30 ml) was then added to the supernatant solution and any precipitate produced was centrifuged, rinsed in acetone, dried and identified by melting point and infrared spectrum. The residual solution and washings were evaporated in a rotary evaporator and acetone (30 ml) was then added to the residue and any further precipitate was treated as before.

After further solvent evaporation, the final residue was confirmed as starting material in all cases by its infrared spectrum.

REFERENCES

1 H. Akagi and Y. Sakagami, *Koshu Eiseiin Kenkyu Hokoku*, 20 (1971) 1; *Chem. Abstr.*, 77 (1972) 48591.
2 P. Dunn and D. Oldfield, *J. Macromol. Sci., Chem.*, A4 (1970) 1157.
3 K. Bürger, *Z. Anal. Chem.*, 192 (1962) 280.