Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

AN INCLUSION COMPOUND FROM HEXAPHENYLDITIN AND TETRAPHENYLTIN

W. R. McWHINNIE*, R. C. POLLER AND M. THEVARASA
Chemistry Department, Queen Elizabeth College, Campden Hill Road, London, W. 8 (Great Britain)

(Received September 2nd, 1967)

In the course of experiments to prepare compounds containing 2-pyridyltin groups it was found that 2-pyridylmagnesium bromide (prepared by the entrainment method with ethyl bromide from 2-bromopyridine in ether) reacted normally with a benzene solution of tributyltin chloride to give tributyl-2-pyridyltin.

When, however, the tributyltin chloride was replaced by triphenyltin chloride a different reaction occurred and no triphenyl-2-pyridyltin was isolated. The product was a colourless crystalline solid m.p. 196–197°, the analysis of which indicated the presence of carbon, hydrogen and tin only. The IR and PMR spectra indicated that only phenyltin groups were present and the absence of ethyl groups was confirmed when the same product was obtained using either methyl iodide or propyl bromide in place of ethyl bromide as the entrainment reagent. The Mössbauer spectrum showed a single peak with a chemical shift of 1.3 ± 0.1 mm/sec relative to SnO_2, that is, within experimental error, the same as the chemical shifts reported for hexaphenylditin and tetraphenyltin[1]. Structure assignment appeared difficult since all the known phenyltin compounds have higher melting points and repeated analyses indicated a ratio of fractionally more than 3 phenyl groups per tin atom.

Limited solubility restricted the methods available for molecular weight determination and a value of 550 was obtained by ebulliometry in carbon tetrachloride; this value can only be regarded as approximate since boiling with carbon tetrachloride appeared to cause decomposition and small amounts of tetraphenyltin were deposited.

The presence of tin–tin bonds in the compound was shown by the rapid decolourisation of a chloroform solution of iodine at room temperature and quantitative studies of iodine cleavage gave an equivalent weight of 475. The major product of iodine cleavage was triphenyltin iodide but some tetraphenyltin was also isolated from the reaction mixture. It was concluded that the substance is an inclusion compound containing hexaphenylditin and tetraphenyltin in the ratio 1.75 : 1; when a mixture of these two substances was heated in nitromethane the same product m.p. 196–197° was obtained.

It is known, for example, that hexaphenylditin crystallises from benzene with solvent of crystallisation but these solvates are not stable[2]. Attempts to form inclusion compounds from triphenyltin chloride, diphenyltin dichloride, triphenylphosphine,

---

* Present address: The Chemistry Department, The University of Aston, Gosta Green, Birmingham 4, (Great Britain).

diphenylmethane and biphenyl with hexaphenylditin were unsuccessful. However, the isomorphous tetraphenylsilane and tetraphenylgermane gave inclusion compounds with hexaphenylditin which had the same melting points and mixed melting points as the tetraphenyltin compound. The Mössbauer spectrum of the tetraphenylsilane compound was similar to that of the tetraphenyltin compound.

Tamborski and Soloski[3] have reported that triphenyltin chloride undergoes a coupling reaction with magnesium in tetrahydrofuran to give hexaphenylditin which then slowly reacts with magnesium to give bis(triphenyltin)magnesium. On hydrolysis the latter compound gives triphenyltin hydride which is known[4] to decompose to tetraphenyltin so that the two components of our inclusion compound are expected to be present in the reaction mixture. Tamborski and Soloski did not observe any reaction in ether but in our experiments the ether was displaced with benzene and it is also possible that the 2-bromopyridine exerted some catalytic effect since, when this was omitted, only hexaphenylditin was isolated.

It appears that, in the presence of magnesium and 2-pyridylmagnesium bromide, triphenyltin chloride reacts preferentially with the metal and tributyltin chloride with the Grignard reagent.

EXPERIMENTAL

Infrared spectra were recorded with the compounds as Nujol mulls using Perkin Elmer 237 and Grubb Parsons DM4 spectrometers. Molecular weights were determined with a semi-micro ebulliometer using carbon tetrachloride as solvent. The Mössbauer spectrometer was a mechanically driven constant velocity apparatus with a $^{119}SnO_2$ source, measurements were carried out with the specimen at liquid nitrogen temperature. PMR measurements were made with a Perkin–Elmer R10 60Mc instrument using deuterochloroform as solvent.

The solvents used for the Grignard reactions were dried over sodium.

Tributyl-2-pyridyltin

Magnesium (1.5 g) and a solution of ethyl bromide (0.1 ml) in ether (5 ml) was placed in a flask fitted with a reflux condenser and mechanical stirrer and a crystal of iodine was added to initiate the reaction. A solution containing 2-bromopyridine (2.9 ml) and ethyl bromide (1 ml) in ether (25 ml) was added at a rate which maintained steady boiling and the mixture was then heated under reflux for 2 h. After cooling, a solution of tributyltin chloride (12.0 g) in benzene (30 ml) was added, the ether was distilled off, more benzene (50 ml) added and the mixture refluxed for 2 h. Excess Grignard reagent was decomposed by the addition of saturated aqueous ammonium chloride and, after filtration, the benzene layer was separated and evaporated to give an oil (7.0 g). An initial distillation gave tributyl-2-pyridyltin (5.33 g) b.p. 116–120°/0.2 mm which on fractional distillation gave an analytical specimen b.p. 140–145°/0.3 mm. (Found: C, 55.5; H, 8.45; N, 3.7. $C_{17}H_{31}NSn$ calcd.: C, 55.5; H, 8.5; N, 3.8%.)

Attempted preparation of triphenyl-2-pyridyltin

When the above experiment was repeated using exactly the same conditions but replacing the tributyltin chloride by triphenyltin chloride (12.3 g) the product was the 1.75 : 1 hexaphenylditin/tetraphenyltin inclusion compound (4.5 g) m.p. 190–192°, raised on crystallisation from nitromethane to 196–197°. (Found: C, 63.2; H, 4.3; Sn, 32.2; mol.wt., 550, eq.wt. (iodine titration) 475. $[C_{36}H_{30}Sn_2]_{1.75}\cdot[C_{24}H_{20}Sn]$ calcd.: C, 63.3; H, 4.4; Sn, 32.3%; expected apparent mol.wt., 601; eq.wt., 472.) Principal IR absorption bands: 1484s, 1435s, 1080s, 1028m, 1002s, 730s, 700s, 452m, 442s, 268s, 262s, these are essentially the same as those shown by tetraphenyltin and hexaphenylditin[5,6]. The PMR spectrum consisted of one multiplet band centred at $\tau = 2.6$.

When the preparation was carried out in the absence of 2-bromopyridine the only tin-containing product isolated was hexaphenylditin (2.9 g) m.p. 227–229°, mixed m.p. with an authentic specimen 228–230°.

Reaction between hexaphenylditin and the tetraphenyl derivatives of tin, silicon and germanium

A mixture of hexaphenylditin (0.40 g, 0.00057 mole), tetraphenyltin (0.12 g, 0.00028 mole) and nitromethane was boiled under reflux for 2 h. The resulting solution on cooling gave crystals of the inclusion compound (0.42 g, 81%) m.p. 194–195°, raised on recrystallisation from nitromethane to 196–197°, this material was identical in all respects with that obtained above.

In an identical manner the hexaphenylditin/tetraphenylsilane inclusion compound was formed in 81% yield m.p. 195–197° unchanged on admixture with the tetraphenyltin compound (Found: C, 66.8; H, 4.75. $[C_{36}H_{30}Sn_2]_{1.75}\cdot[C_{24}H_{20}Si]$ calcd.: C, 66.9; H, 4.7%.)

The corresponding tetraphenylgermane inclusion compound was prepared similarly in 76% yield m.p. 197–199°, mixed m.p. with the tetraphenyltin compound 194–196°. (Found: C, 64.3; H, 4.6. $[C_{36}H_{30}Sn_2]_{1.75}\cdot[C_{24}H_{20}Ge]$ calcd.: C, 65.1; H, 4.6%.)

Reaction of the hexaphenylditin/tetraphenyltin inclusion compound with iodine

A 0.05 *N* solution of iodine in chloroform was added dropwise to a solution of the inclusion compound (0.48 g) in chloroform (10 ml) until a faint iodine colour persisted. The solvent was evaporated off and the residue extracted with boiling light petroleum (b.p. 60–80°). On cooling the extract deposited crystals of triphenyltin iodide (0.32 g) m.p. 120° (lit.[7] m.p. 121°). The material which was insoluble in light petroleum was recrystallised from xylene to give tetraphenyltin (0.045 g) m.p. 224° (lit.[8] m.p. 225–226°). The identifications of these two products were confirmed by mixed m.p. and IR determinations.

ACKNOWLEDGEMENTS

We thank the Science Research Council for a grant for the Mössbauer spectrometer and Prof. G. J. M. VAN DER KERK (Institute for Organic Chemistry, T.N.O., Utrecht) for a gift of tetraphenylgermane.

SUMMARY

Although tributyltin chloride reacted normally with 2-pyridylmagnesium bro-

mide to give tributyl-2-pyridyltin, the corresponding reaction with triphenyltin chloride did not occur. Instead an inclusion compound was isolated consisting of hexaphenylditin and tetraphenyltin in the ratio 1.75 : 1. Tetraphenylsilane and tetraphenylgermane also form inclusion compounds with hexaphenylditin.

REFERENCES

1 T. C. Gibb and N. N. Greenwood, *J. Chem. Soc., A*, (1966) 43.
2 E. Krause and R. Becker, *Ber.*, 53 (1920) 173.
3 C. Tamborski and E. J. Soloski, *J. Amer. Chem. Soc.*, 83 (1961) 3734.
4 K. Moedritzer, *Organometal. Chem. Rev.*, 1 (1966) 227.
5 R. C. Poller, *J. Inorg. Nucl. Chem.*, 24 (1962) 593.
6 R. C. Poller, *Spectrochim. Acta.*, 22 (1966) 935.
7 E. Krause, *Ber.*, 51 (1918) 912.
8 A. Polis, *Ber.*, 22 (1889) 2915.