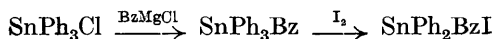


CCCXII.—*An Attempt to prepare Optically Active Derivatives of Quadrivalent Tin.*

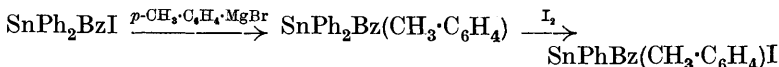
By FREDERIC BARRY KIPPING.

THE only optically active compound of tin hitherto described is that of Pope and Peachey (P., 1900, **16**, 42, 116), who obtained externally compensated methylethyl-*n*-propylstannic iodide, and hence prepared both the *d*-camphorsulphonate and the *d*- α -bromo- π -camphorsulphonate. Evaporation of aqueous solutions of these salts produced in each case salts of the dextrorotatory base only, the whole of the lævorotatory base being converted into its dextrorotatory isomeride. From these salts was isolated *d*-methylethyl-*n*-propylstannic iodide, having $[\alpha]_D = +23^\circ$ in ethereal solution. Furthermore, *d*-methylethyl-*n*-propylstannic *d*- α -bromo- π -camphorsulphonate was found to be completely racemised by heating in aqueous solution on the water-bath for 2 hours, such a solution again giving the dextrorotatory salt on evaporation to dryness.

In view of these results it appeared to be of interest to attempt the preparation of further optically active derivatives of tin in order to ascertain if the remarkable mobility of the groups attached to this atom persisted in all its compounds. The aromatic derivatives were chosen for this investigation, as being more readily crystallised and possibly less easily racemised than the aliphatic compounds. The proposed method of preparation was that of Pope and Peachey, *i.e.*, to start with a triarylstannic halide, introduce a different aryl group by means of the Grignard reagent and remove one of the three original radicals by treatment with iodine :



A third aryl group was then to be introduced and one of the two like radicals again removed,



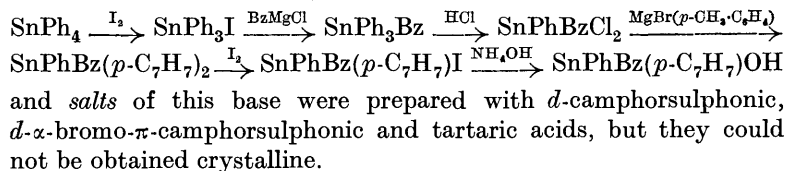
As a preliminary, it was therefore decided to prepare some mixed tin-aryls and study the action of iodine on these compounds in order to determine in which order the various groups must be introduced into the molecule for the above purpose.

The only available data on this subject are that treatment of a benzyl-alkyl compound with iodine results in the elimination of a benzyl group (Smith and Kipping, J., 1912, **101**, 2553), and that one of the phenyl groups is similarly removed from *cyclohexyltriphenylstannane* (Krause and Pohland, *Ber.*, 1924, **57**, 544).

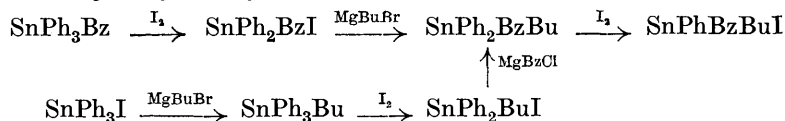
In the present instance, it was found that the ease with which various groups were removed by iodine from a molecule containing two or three different radicals decreased in the following order: *o*-tolyl, *p*-tolyl, phenyl, benzyl. Thus triphenyl-*p*-tolylstannane with iodine gave triphenylstannic iodide and *p*-iodotoluene, but *triphenylbenzylstannane* yielded diphenylbenzylstannic iodide and iodobenzene. The tin aryls are also decomposed by boiling with concentrated hydrochloric acid, and it was found that this reagent often removed two aryl groups.

For example, triphenylbenzylstannane yields *phenylbenzylstannic chloride* and benzene, whilst tetraphenylstannane gives diphenylstannic chloride. The order in which the groups were removed by hydrochloric acid was the same as that with iodine, except that, whereas iodine removes one of the benzyl radicals from tribenzylethylstannane, hydrochloric acid removes the ethyl group.

Phenylbenzyl-p-tolylstannic hydroxide was then prepared by the following series of reactions:

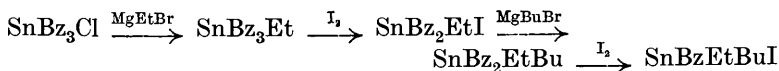


Phenylbenzyl-n-butylstannic iodide was then prepared:



but again the salts, with the exception of the *fluoride*, proved to be oils. It was then thought that the aromatic nucleus directly

attached to the tin atom might be the cause of the failure of the salts to crystallise, and a third compound, *benzylethyl-n-butylstannic iodide*, was prepared in which no nucleus is thus attached :



Here again the salts resisted all attempts at crystallisation.

EXPERIMENTAL.

Phenyltribenzylstannane.—To a solution of phenyl magnesium bromide (2 mols.) in ether was added tribenzylstannic chloride (1 mol.) (J., 1912, **101**, 2556), and the mixture heated on the water bath for $\frac{1}{2}$ hour. The ether was then removed by distillation and the heating continued for a further $1\frac{1}{2}$ hours. The product was treated with water, distilled in steam, and the residual oil extracted with ether, dried, and distilled in a vacuum, b. p. $290^\circ/5$ mm.* (Found : C, 69.4; H, 5.5. $\text{C}_{27}\text{H}_{26}\text{Sn}$ requires C, 69.1; H, 5.5 %). *Phenyltribenzylstannane* does not solidify at 0° and is miscible with all the ordinary solvents, with the exception of alcohol; it is converted by boiling concentrated hydrochloric acid into tribenzylstannic chloride and benzene.

Tribenzylstannic iodide was obtained from tribenzylstannic hydroxide (*Z. anorg. Chem.*, 1910, **68**, 102) by warming with dilute hydriodic acid; it crystallises easily from glacial acetic acid in glistening, needle-like prisms, m. p. $102\text{--}103^\circ$ (Found : I, \dagger 24.3; Sn, 22.7. $\text{C}_{21}\text{H}_{21}\text{ISn}$ requires I, 24.5; Sn, 22.9%). The same compound was obtained by treatment of phenyltribenzylstannane (1 mol.) dissolved in carbon tetrachloride with iodine (1 mol.), removal by steam-distillation of the solvent and iodobenzene, and crystallisation from acetic acid.

Dibenzylstannic Chloride.—Attempts to prepare benzylstannic chloride by treatment of tribenzylstannic chloride with 2 mols. of iodine resulted in failure, as only one benzyl group could be removed in this way; the product, isolated in the usual way and converted from iodide into chloride, proved to be dibenzylstannic chloride, m. p. 158° .

Tetraphenylstannane was prepared in quantity by a modification of the method of Pfeiffer and Schnurmann (*Ber.*, 1904, **37**, 319). Stannic chloride (100 g.) was slowly added to absolute ether (440 c.c.) which was cooled in ice and stirred mechanically. Magnesium

* The pressures given in this paper are probably only accurate to 2—3 mm.

† All halogen determinations were carried out by dissolving the material in alcohol, adding excess of *N*/10-silver nitrate and titrating the excess with potassium thiocyanate.

(36.8 g.) was then added and bromobenzene (244 g.) dropped in slowly. After the addition of the first 10 c.c. or so, a crystal of iodine was added to start the reaction, the mixture being warmed if necessary. The bromobenzene was afterwards added at such a rate that the mixture, still cooled in ice and stirred well, boiled gently. Addition occupied about 1 hour, and the product was then heated on the water-bath for 2 hours, the ether distilled away, and heating continued for a further 2 hours. The solid residue was then added to cold water, acidified with hydrochloric acid, and filtered. The solid, after drying in air, was boiled with about 600 c.c. of xylene and the solution filtered hot. Tetraphenylstannane crystallised from the filtrate in slender needles and was recrystallised from the same solvent; yield about 50—55%.

Triphenylstannic Chloride.—Attempts to prepare this substance directly from stannic chloride (1 mol.) and phenyl magnesium bromide (3 mols.) by a method similar to that used for tribenzylstannic chloride (J., 1912, **101**, 2556) yielded tetraphenylstannane as the principal product, with only small amounts of the halogen compound; the method of Chambers and Scherer (*J. Amer. Chem. Soc.*, 1926, **48**, 1055) was finally found to be best for the preparation of both the chloride and iodide: Tetraphenylstannane was boiled with hydrochloric acid for about 10 mins. and the oily product extracted with petroleum; on standing, a solid mass of diphenylstannic chloride, m. p. 42°, was produced from which, by boiling with water, diphenylstannic hydroxychloride, m. p. 187°, could be prepared.

Triphenylbenzylstannane was prepared from triphenylstannic iodide and benzyl magnesium chloride in the usual manner. After removal of impurities by distillation in steam, the product solidified, and then crystallised from alcohol in beautiful colourless plates, m. p. 90°, b. p. 250°/3 mm. (Found: C, 67.9; H, 5.04; Sn, 26.5. $C_{25}H_{22}Sn$ requires C, 68.1; H, 5.0; Sn, 27.0%). The substance is readily soluble in the usual solvents with the exception of alcohol.

Phenylbenzylstannic Chloride.—Triphenylbenzylstannane (1 mol.) in chloroform was treated with iodine (1 mol.), which was added gradually as the colour was discharged. After removal of the solvent and iodobenzene by distillation either in steam or under diminished pressure, an oil remained which could not be obtained crystalline. It was therefore treated with ammonia, and the resultant hydroxide warmed with dilute hydrochloric acid. On cooling, a solid was produced which crystallised from petroleum (b. p. 80—100°) in colourless needles, m. p. 83—84° (Found: C, 43.98; H, 3.4; Cl, 19.6. $C_{13}H_{12}SnCl_2$ requires C, 43.6; H, 3.4; Cl, 19.8%). Here, apparently, the gentle warming with hydro-

chloric acid has been sufficient to remove one of the phenyl groups from the molecule. *Phenylbenzylstannic chloride* was also produced by warming triphenylbenzylstannane with concentrated hydrochloric acid for a few minutes—prolonged boiling results in the complete breakdown of the molecule, stannous chloride being formed.

Tribenzyl-p-tolylstannane was prepared from tribenzylstannic chloride and *p*-tolyl magnesium bromide in the usual way. It does not solidify at 0°, and treatment with iodine or hydrochloric acid results in the formation of tribenzylstannic iodide or chloride respectively.

Triphenyl-*p*-tolylstannane (*Ber.*, 1919, **52**, 2150), on treatment with iodine and conversion of the iodide into chloride, yielded triphenylstannic chloride.

Triphenyl-o-tolylstannane, from triphenylstannic iodide and *o*-tolyl magnesium bromide, crystallised easily from diacetone-alcohol or petroleum in stout, colourless needles, m. p. 165° (Found : C, 67·6; H, 5·4; Sn, 26·7. $C_{25}H_{22}Sn$ requires C, 68·1; H, 5·0; Sn, 27·0%). Treatment with iodine resulted in the formation of *o*-iodotoluene and triphenylstannic iodide. Boiling with hydrochloric acid for a few seconds similarly gave toluene and triphenylstannic chloride.

Tetra-*p*-tolylstannane (*Z. anorg. Chem.*, 1910, **68**, 122) on treatment with 1 mol. of iodine in chloroform yielded tri-*p*-tolylstannic iodide (*Ber.*, 1920, **53**, 183). Boiling hydrochloric acid converted tetra-*p*-tolylstannane into an oil which was extracted with petroleum; after prolonged standing, crystals, m. p. 38–40°, were formed, which were doubtless di-*p*-tolylstannic chloride (*J.*, 1913, **103**, 2049).

Tri-p-tolyl-o-tolylstannane, prepared as usual from tri-*p*-tolylstannic chloride and *o*-tolyl magnesium bromide, crystallised readily from petroleum in colourless prisms, m. p. 168° (Found : Sn, 24·5, 24·65. $C_{28}H_{28}Sn$ requires Sn, 24·65%). It is readily soluble in benzene and chloroform, fairly so in hot acetone, and not very readily in alcohol. Treatment with iodine results in the formation of *o*-iodotoluene and tri-*p*-tolylstannic iodide.

Tri-m-tolylstannic Chloride.—Treatment of tetra-*m*-tolylstannane (*Ber.*, 1920, **53**, 184) with 1 mol. of iodine resulted in the production of an oily iodide which was decomposed with ammonia and then treated with dilute hydrochloric acid; the *chloride* crystallised easily from alcohol or petroleum in small, colourless prisms, m. p. 108–109° (Found : Cl, 8·2. $C_{21}H_{21}SnCl$ requires Cl, 8·3%).

Tri-m-tolyl-p-tolylstannane, from tri-*m*-tolylstannic chloride and *p*-tolylmagnesium bromide, crystallised from alcohol in minute, colourless needles, m. p. 103° (Found : Sn, 24·8. $C_{28}H_{28}Sn$ requires Sn 24·65%). Treatment with iodine resulted in the formation of an

iodide which could not be obtained pure and was probably a mixture of tri-*m*-tolylstannic and di-*m*-tolyl-*p*-tolylstannic iodides. The iodotoluene evolved would not solidify and was probably a mixture of the *o*- and *p*-isomerides.

Phenyldi-p-tolylbenzylstannane was prepared by addition of phenylbenzylstannic chloride to excess of *p*-tolyl magnesium bromide; it has b. p. 265—270°/2—3 mm. and does not solidify (Found: C, 69·2; H, 5·6. C₂₇H₂₆Sn requires C, 69·1; H, 5·55%). It is readily soluble in the usual solvents with the exception of methyl and ethyl alcohols. Treatment with boiling hydrochloric acid resulted in the expulsion of the two tolyl groups and formation of phenylbenzylstannic chloride.

Phenyl-p-tolylbenzylstannic Hydroxide.—Attempts to prepare salts of this base by treatment of phenylbenzylstannic chloride with 1 mol. of *p*-tolyl magnesium bromide resulted in failure, phenyldi-*p*-tolylbenzylstannane being formed and some of the halide remaining unattacked; but treatment of phenyldi-*p*-tolylbenzylstannane in chloroform solution with 1 mol. of iodine resulted in elimination of *p*-iodotoluene and formation of an oily *iodide*. This salt was therefore treated with ammonia and a solid *hydroxide* produced, which after three crystallisations from ethyl acetate melted at 136—137° (Found: C, 60·98; H, 5·14; Sn, 30·1. C₂₀H₂₀OSn requires C, 60·8; H, 5·07; Sn, 30·1%). The *d-camphorsulphonate* of this base was obtained by dissolving equimolecular proportions of it and the acid in acetone. Evaporation of the solvent left an oil which resisted all attempts at crystallisation. It was readily soluble in acetone, alcohol, ethyl acetate, and chloroform, but almost insoluble in water and petroleum. Solution in acetone followed by precipitation by water was carried out six times, but the product was still oily, and the base recovered from the salt optically inactive. The *d-α-bromo-π-camphorsulphonate*, prepared by dissolving the base in an equivalent quantity of the acid in alcoholic solution, was also oily; it is readily soluble in ether, sparingly so in alcohol, and almost insoluble in water. After fractional precipitation of an acetone solution by addition of water, the salt still resisted crystallisation, and the base recovered from it was optically inactive. The *d-tartrate* was an amorphous solid almost insoluble in the usual solvents, with the exception of alcohol; fractional precipitation of an alcoholic solution by addition of petroleum produced no change in the properties of the salt and the recovered base was optically inactive.

Triphenyl-n-butylstannane, prepared in the usual manner from triphenylstannic iodide and *n*-butyl magnesium bromide, crystallises readily from hot alcohol in colourless needles, m. p. 61—62°, b. p.

222°/3 mm. (Found : Sn, 28·9; 29·7. $C_{22}H_{24}Sn$ requires Sn, 29·3%), and is readily soluble in petroleum, ethyl acetate, and benzene. Boiling with hydrochloric acid for a few seconds converts this compound into *phenyl-n-butylstannic chloride*, crystallising from light petroleum (b. p. 40—60°) in colourless prisms, m. p. 50° (Found : C, 37·12; H, 4·39; Cl, 21·4. $C_{10}H_{14}SnCl_2$ requires C, 37·0; H, 4·32; Cl, 21·9%).

Diphenylbenzyl-n-butylstannane.—Triphenylbenzylstannane (1 mol.) in chloroform was treated with iodine (1 mol.), and after completion of the reaction, the solvent and iodobenzene were removed by distillation under reduced pressure. To the oily *iodide* produced in this manner was added an ethereal solution of *n*-butyl magnesium bromide ($1\frac{1}{2}$ mols.); the product was worked up as usual and a colourless oil isolated, b. p. 215°/2—3 mm. (Found : Sn, 28·5, 28·3. $C_{23}H_{26}Sn$ requires Sn, 28·3%). This compound was also prepared by treatment of triphenylbutylstannane successively with iodine and benzyl magnesium chloride.

Phenylbenzyl-n-butylstannic Hydroxide.—Diphenylbenzylbutylstannane was treated with 1 mol. of iodine in chloroform solution, and the solvent evaporated. Distillation of the residue under reduced pressure yielded an iodide, b. p. 185—189°, which was clearly iodobenzene, and left an oil which was converted into a solid *hydroxide* by treatment with ammonia; crystallisation twice from benzene and then twice from alcohol gave a product, m. p. 135—137° (not sharp) (Found : Sn, 33·0. $C_{17}H_{22}OSn$ requires Sn, 33·0%). Although the chloride, bromide, and iodide of this base were oils, a crystalline *fluoride* was precipitated by addition of an aqueous solution of neutral potassium fluoride to the base dissolved in alcohol and acetic acid; the product crystallised from alcohol in colourless needles, m. p. 218° (Found : C, 56·3; H, 5·9. $C_{17}H_{21}SnF$ requires C, 56·3; H, 5·8%).

The *d-camphorsulphonate* of phenylbenzyl-*n*-butylstannic hydroxide was formed both by dissolution of the base in an acetone solution of the acid and by double decomposition of the iodide with silver *d*-camphorsulphonate. The salt could not, however, be obtained solid even after fractional precipitation of an acetone solution with water; the *d-α-bromo-π-camphorsulphonate* and the *d-camphorate* were also persistently oily. The *d-tartrate* was an amorphous solid which did not melt at 250°, but melted under hot alcohol; it was dissolved in this solvent and allowed to separate again several times, and the alcoholic solution was then precipitated with aqueous potassium fluoride, but the fluoride so formed was optically inactive in alcoholic solution.

Tribenzylethylstannane is decomposed by iodine with the elimin-

ation of one of the benzyl groups (J., 1912, **101**, 2553). On the other hand, it was found that hydrochloric acid acts on this substance only with extreme slowness, and after an hour's heating under reflux a solid product was obtained which proved to be tribenzylstannic chloride.

Dibenzylethyl-n-butylstannane, prepared from tribenzylethylstannane in an exactly similar manner to the preparation of diphenylbenzyl-*n*-butyl- from triphenylbenzylstannane, is a colourless oil, b. p. 195—200°/3—5 mm. (Found: C, 61.6; H, 7.5. $C_{20}H_{28}Sn$ requires C, 62.0; H, 7.3%).

Salts of Benzylethyl-n-butylstannic Hydroxide.—Treatment of dibenzylethyl-*n*-butylstannane with 1 mol. of iodine gave an oily *iodide* which was dissolved in alcohol and treated with one equivalent of silver *d*-camphorsulphonate in water; the silver iodide was removed by filtration and the filtrate evaporated, but the resulting oil could not be crystallised. Similar results were obtained by using silver *d*- α -bromo- π -camphorsulphonate.

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