Functionally Substituted Organotin Compounds. Part IV.[1] The Use of Protecting Groups in the Formation of 4-Oxopentyltin Compounds

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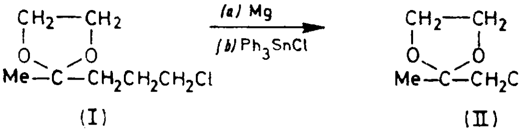
Protection of the carbonyl group in 1-chloropentan-4-one by dioxolan formation has enabled preparation of a series of 4-oxopentyltin compounds *via* the Grignard reagent. I.r., n.m.r., and Mössbauer spectroscopy have been used to aid structure assignments: in many of the compounds the carbonyl group is intramolecularly co-ordinated to tin. Stereochemical assignments have been made for (4-oxopentyl)diphenyltin chloride and di(4-oxopentyl)tin dibromide.

As part of an investigation into new methods of preparation of functionally substituted organotin compounds,[1-3] we now report the successful use of protecting groups in the preparation of 4-oxopentyltin compounds.

RESULTS AND DISCUSSION

Protection of the carbonyl group in 1-chloropentan-4-one was achieved by conversion to 2-(3-chloropropyl)-2-methyl-1,3-dioxolan, (I), which readily formed a Grignard reagent. The latter reacted with triphenyltin chloride to give the 2-methyl-2-[(3-triphenylstannyl)propyl]-1,3-dioxolan, (II). Initial attempts to remove the protecting ethylenedioxy-residue from compound (II) using hydrochloric acid were only partially successful in that the reaction was always accompanied by fission of phenyl–tin bonds. Treatment of compound (II) with 6M-hydrochloric acid gave (4-oxopentyl)diphenyltin chloride, (III), while use of 10M-HCl gave (4-oxopentyl)phenyltin dichloride, (IV). Carbon–tin bond cleavage was avoided by treating compound (II) with acetone and *p*-toluenesulphonic acid to give (4-oxopentyl)triphenyltin, (V).



(I) (II)

In a similar manner reaction between the Grignard reagent from (I) and diphenyltin dichloride gave a product from which di(4-oxopentyl)diphenyltin, (VI), and di(4-oxopentyl)tin dichloride, (VII), were obtained. Treatment of compound (VI) with bromine gave di(4-oxopentyl)tin dibromide, (VIII); both (VII) and (VIII) gave crystalline 1 : 1 adducts with 2,2′-bipyridyl (bipy). When the same Grignard reagent was treated with tin(IV) chloride the expected product with four substituted pentyl groups attached to tin was obtained, but attempts to remove the protecting ethylenedioxy-residues did not give a pure product.

The positions of the ν(C=O) bands in the i.r. spectra of these products are shown in the Table, from which it is clear that the carbonyl group is co-ordinated to tin in compounds (III), (IV), (VII), and (VIII), but not in (V) and (VI) because of the reduced Lewis acidity of tin in these compounds.[4] On conversion of compounds (IV), (VII), and (VIII) to their bipy adducts, the co-ordination bonds from oxygen to tin are broken and the ν(C=O)

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[1] Part III, G. Ayrey, J. R. Parsonage, and R. C. Poller, *J. Organometallic Chem.*, 1973, **56**, 193.

[2] G. Ayrey, R. D. Brasington, and R. C. Poller, *J. Organometallic Chem.*, 1972, **35**, 105.

[3] R. D. Brasington and R. C. Poller, *J. Organometallic Chem.*, 1972, **40**, 115.

[4] R. C. Poller, 'The Chemistry of Organotin Compounds,' Logos Press, London, 1970, p. 185.

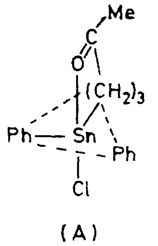
bands revert to positions characteristic of free carbonyl groups. Further evidence of co-ordination through the carbonyl oxygen atom was obtained from chemical shifts of the methylenic protons adjacent to the carbonyl group (Table). In compounds (V) and (VI) these methylenic protons resonated at τ 7·55; replacement of the phenyl by halide groups in these compounds caused downfield shifts because co-ordination of the oxygen atoms to tin reduces the shielding of these protons. Again, conversion of compounds (IV), (VII), and (VIII) to their bipy adducts frees the carbonyl groups and proton signals from the $-CH_2CO-$ group revert to τ 7·55.

I.r. (cm^{-1}), n.m.r. (τ), and Mössbauer (mm s^{-1}) spectral parameters

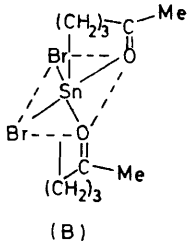
Compounds	ν(C=O) [a]	τ [b] ($-CH_2CO-$)	δ [c]	Δ
$Ph_3SnCH_2CH_2CH_2COMe$ (V)	1 705 [d]	7·55	1·73	0
$Ph_2ClSnCH_2CH_2CH_2COMe$ (III)	1 669	7·46	1·38	−3·30 [e]
$PhCl_2SnCH_2CH_2CH_2COMe$ (IV)	1 670	7·30		
$PhCl_2SnCH_2CH_2CH_2COMe$,bipy [f]	1 710	7·55		
$Ph_2Sn(CH_2CH_2CH_2COMe)_2$ (VI)	1 709	7·55	1·41	0
$Cl_2Sn(CH_2CH_2CH_2COMe)_2$ (VII)	1 680	7·23		
$Cl_2Sn(CH_2CH_2CH_2COMe)_2$,bipy [f]	1 705	7·42		
$Br_2Sn(CH_2CH_2CH_2COMe)_2$ (VIII)	1 675	7·27	1·66	+3·83 [e]
$Br_2Sn(CH_2CH_2CH_2COMe)_2$,bipy [f]	1 703	7·55	1·56	+3·80 [g]

[a] Compound (VI) was measured as a liquid film, the others as Nujol mulls. [b] Compound (V) was measured in carbon tetrachloride, the others in deuteriochloroform. [c] Relative to tin(IV) oxide. [d] *Cf.* $Me_3SnCH_2CH_2CH_2COMe$ which shows ν(C=O) at 1 710 cm^{-1} (H. G. Kuivila, K. H. Tsai, and P. L. Maxfield, *J. Amer. Chem. Soc.*, 1970, **92**, 6696). [e] Sign determined by measuring spectrum in a magnetic field (see ref. 5). [f] bipy = 2,2′-Bipyridyl. [g] Sign of quadrupole splitting was assumed.

Two of the compounds, (III) and (VIII), were selected for more complete structure determination; molecular-weight measurements showed them to be monomeric so that the tin-oxygen bonding is intramolecular. The Mössbauer spectrum of compound (V) was a singlet characteristic of four-co-ordinate organotin compounds; the spectrum of (III) was a doublet, with a quadrupole splitting of −3·30 mm s^{-1}, the minus sign indicating[5] structure (A) for this compound. Similarly, although compound (VI) with four Sn–C bonds showed the expected singlet Mössbauer spectrum, the dibromo-compound (VIII) exhibited quadrupole splitting, the magnitude[6] and sign[5] of which indicate *trans*-organic groups. The close correspondence between the Mössbauer parameters of (VIII) and its bipy derivative suggest that compound (VIII) has structure (B).



(A)



(B)

EXPERIMENTAL

I.r. spectra were measured on Nujol mulls; n.m.r. spectra were measured in deuteriochloroform or carbon tetrachloride. The Mössbauer spectrometer has been described previously;[7] measurements were made with the samples at 78 K and isomer shifts refer to tin(IV) oxide. Mössbauer measurements in a magnetic field, and the assignment of the sign of the quadrupole splitting, were carried out by the P.C.M.U. service at Harwell. Molecular-weight measurements were carried out osmometrically in benzene.

Preparations.— 2-*Methyl*-2-[(3-*triphenylstannyl*)*propyl*]-1,3-*dioxolan*, (II). Triphenyltin chloride (38·5 g, 0·10 mol) in tetrahydrofuran (200 cm^3) was added to the Grignard reagent, prepared from 2-(3-chloropropyl)-2-methyl-1,3-dioxolan,[8] (I) (45·0 g, 0·27 mol), and magnesium (8·02 g, 0·33 mol) in tetrahydrofuran (200 cm^3), and the mixture boiled under reflux for 2 h. Hydrolysis using saturated aqueous ammonium chloride and normal work-up gave, from light petroleum (b.p. 60—80 °C), the colourless crystalline *product* (18·8 g), m.p. 52—54 °C (Found: C, 62·7; H, 6·0. Calc. for $C_{25}H_{28}O_2Sn$: C, 62·7; H, 5·8%).

(4-*Oxopentyl*)*triphenyltin*, (V). Compound (II) (9·5 g) and *p*-toluenesulphonic acid (0·20 g) in dry acetone (120 cm^3) was boiled under reflux for 14 h. The solution was concentrated to 50 cm^3, water (80 cm^3) added, and the mixture extracted with diethyl ether. The diethyl ether extracts, after washing with dilute sodium hydrogen carbonate, gave the *product* (6·20 g), m.p. 37—40 °C. The product was crystallised from light petroleum (b.p. 60—80 °C), m.p. 42—44 °C (Found: C, 63·5; H, 5·8. Calc. for $C_{23}H_{24}OSn$: C, 63·5; H, 5·5%).

Treatment of compound (II) *with hydrochloric acid*. (a) Compound (II) (2·53 g) in light petroleum (100 cm^3) and hydrochloric acid (6M, 100 cm^3) was shaken for 5 h. The organic layer, after washing with dilute aqueous sodium hydrogen carbonate, gave from ethanol colourless crystals of (4-*oxopentyl*-O)*diphenyltin chloride*, (III) (1·58 g), m.p. 108—110 °C (unchanged on further crystallisation) (Found: C, 52·1; H, 5·1; *M*, 397. Calc. for $C_{17}H_{19}ClOSn$: C, 51·9; H, 4·8%; *M*, 393).

(b) In a similar experiment using 10M-hydrochloric acid for 20 h the product was (4-*oxopentyl*-O)*phenyltin dichloride* (IV), m.p. 102—104 °C (from ethanol) (Found: C, 37·2; H, 4·3. Calc. for $C_{11}H_{14}Cl_2OSn$: C, 37·6; H, 4·0%). Treatment of compound (IV) with 2,2′-bipyridyl (bipy) gave the 1 : 1 *adduct*, m.p. 174—176 °C (Found: C, 49·4; H, 4·6; N, 5·9. Calc. for $C_{21}H_{22}Cl_2N_2OSn$: C, 49·65; H, 4·3; N, 5·5%).

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[5] B. A. Goodman and N. N. Greenwood, *J. Chem. Soc.* (*A*), 1971, 1862.

[6] B. W. Fitzsimmons, N. J. Seeley, and A. W. Smith, *J. Chem. Soc.* (*A*), 1969, 143.

[7] R. C. Poller and J. N. R. Ruddick, *J. Chem. Soc.* (*A*), 1969, 2273.

[8] Cl. Feugeas and H. Normant, *Bull. Soc. chim. France*, 1963, 1441.

Bis[(4,4-*ethylenedioxy*)*pentyl*]*diphenyltin*, (IX). Diphenyltin dichloride (21·30 g) in dry benzene (150 cm^3) was added to the Grignard reagent, prepared from compound (I) (38·3 g) and magnesium (7·29 g) in dry tetrahydrofuran (120 cm^3), and the mixture boiled under reflux for 3 h. Hydrolysis using saturated aqueous ammonium chloride and normal work-up gave the *product* as an oil (28·6 g), n_D^{20} 1·5483. The oil could not be distilled without decomposition and was shown to be homogeneous by thin-layer chromatography (Found: C, 59·4; H, 7·2. Calc. for $C_{26}H_{36}O_4Sn$: C, 58·8; H, 6·8%).

Di(4-*oxopentyl*)*diphenyltin*, (VI.) A solution of compound (IX) (20·0 g) and *p*-toluenesulphonic acid (0·6 g) in dry acetone (250 cm^3) was concentrated to 100 cm^3, water (200 cm^3) added, and diethyl ether extraction gave the viscous liquid *product* (11·6 g). The latter was purified by elution from a silica-gel column with chloroform (65% recovery), n_D^{20} 1·5410 (Found: C, 59·7; H, 7·2. Calc. for $C_{22}H_{28}O_2Sn$: C, 59·6; H, 6·4%).

Di(4-*oxopentyl*-O)*tin dichloride*, (VII). Compound (IX) (3·80 g) in diethyl ether (150 cm^3) and hydrochloric acid (10M, 35 cm^3) was shaken for 20 h. Normal work-up gave the *product* (0·94 g), crystallised from ethanol, m.p. 77—79 °C (Found: C, 33·2; H, 5·2. Calc. for $C_{10}H_{18}Cl_2O_2Sn$: C, 33·4; H, 5·0%). Treatment of compound (VII) with bipy gave the 1 : 1 *adduct*, m.p. 152—154 °C (Found: C, 46·6; H, 5·1; N, 5·2. Calc. for $C_{20}H_{26}Cl_2N_2O_2Sn$: C, 46·6; H, 5·0; N, 5·4%).

Di(4-*oxopentyl*-O)*tin dibromide*, (VIII). Bromine (8·94 g) in dry chloroform (150 cm^3), and compound (VI) (12·5 g) in the same solvent (150 cm^3) at 0 °C gave, after removal of the solvent, the *dibromide* (7·2 g) crystallised from methanol, m.p. 94—96 °C (Found: C, 26·4; H, 4·3; *M*, 519. Calc for $C_{10}H_{18}Br_2O_2Sn$: C, 26·7; H, 4·0%; *M*, 449). Treatment of compound (VIII) with bipy gave the 1 : 1 *adduct*, m.p. 154—156 °C (Found: C, 39·3; H, 4·85; N, 4·6 Calc. for $C_{20}H_{26}Br_2N_2O_2Sn$: C, 39·7; H, 4·3; N, 4·6%).

Tetrakis[(4,4-*ethylenedioxy*)*pentyl*]*tin*. Reaction between tin(IV) chloride (5·21 g), in benzene (150 cm^3), and the Grignard reagent, prepared from compound (I) (24·07 g) and magnesium (4·86 g) in tetrahydrofuran (100 cm^3), followed by hydrolysis using saturated aqueous ammonium chloride gave, after normal work-up, the *product* (7·40 g) as a viscous oil n_D^{20} 1·4950 (Found: C, 52·7; H, 8·3. Calc. for $C_{28}H_{52}O_8Sn$: C, 52·9; H, 8·2%). The Mössbauer spectrum showed a singlet, $\delta = 1·39$ mm s^{-1}, and the expected absorptions were observed in the n.m.r. spectrum.

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