Dissymmetric Tertiary-alkyl Tin(IV) Compounds

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The preparation of some new dissymmetric alkyl compounds of tin(IV) is described, in particular those containing t-butyl and t-pentyl groups. The ^{1}H n.m.r. spectra of these compounds at 100 and 220 MHz has been investigated, and the appearance of magnetic non-equivalence is discussed. A temperature-dependence study of the ^{1}H n.m.r. spectra confirms that the tetra-alkyltin(IV) compounds are stereochemically stable.

SEVERAL asymmetric tetra-alkyltin(IV) compounds with the chiral centre at a carbon atom are known, and ^{1}H n.m.r. studies on several such compounds have been reported.[1,2] The anisochronous behaviour of diastereotopically related protons has been observed in certain types of these compounds. Evidence for such behaviour has also been reported for two tin compounds with chiral tin and asymmetric carbon centres,[3] and for one tetra-alkyltin(IV) compound in which non-equivalence in the ^{1}H n.m.r. spectrum is due to asymmetry at the tin atom.[4] The latter compound, benzyl(methyl)(neophyl)(phenyl)-tin(IV) [neophyl = $Ph(Me)_2CCH_2$] showed anisochronous behaviour of the benzyl methylene protons only. The present investigation was undertaken to study the effect of bulky groups, *e.g.* t-butyl and t-pentyl, on the magnitude of the observed splitting, and to obtain ^{1}H n.m.r. data on rates of inversion of enantiomorphic organotin(IV) compounds. As with other chiral tetra-alkyltin(IV) compounds,[4] magnetic non-equivalence was usually observed in the presence of a neophyl group, supporting the idea that diastereotopic splitting is favoured by the presence of a group with a large magnetic anisotropy. The results of some synthetic studies on t-pentyl compounds of tin are presented. In general it was found that the t-pentyl group exhibits considerably more steric hindrance than the t-butyl group in alkylation reactions of organotin halide compounds. Some distannane compounds resulting from attempted substitutions by t-pentylmagnesium chloride were also obtained.

EXPERIMENTAL

The synthesis of the compounds was accomplished by successive elimination of a phenyl group from tetraphenyltin(IV), followed by appropriate substitutions using the lithium or Grignard reagent of the desired substituent. Solid tetraorganotin(IV) compounds were recrystallized from methanol and dried by pumping *in vacuo* at room temperature. Liquid organotin compounds were purified by elution chromatography using petroleum spirit (b.p. 60—80 °C).

N.m.r. spectra were obtained on a Varian HA 100 MHz instrument using TMS as a reference and dichloromethane as an internal lock signal. The latter was chosen because it places the lock signal *ca.* 5 p.p.m. downfield of TMS, which is a region completely free of proton resonance signals from any of the tin compounds studied. In addition, spectra of the dissymmetric compounds were also obtained at 220 MHz using TMS as a reference. For coupled anisochronous protons, the shifts were calculated using eigenfunctions for a two-spin system.[5] Refractive-index measurements were made on an Abbey refractometer.

RESULTS AND DISCUSSION

The t-Pentyl Group.—The structural requirements for the introduction of a t-butyl group into an organotin compound to give a normal substitution product as opposed to a tin–tin bonded dimer have been discussed previously.[6] In the present study, a preliminary investigation of the structural requirements for the introduction of a t-pentyl radical was undertaken, the reagent t-pentylmagnesium chloride being reacted with a cross section of triorganotin(IV) iodide compounds.

Lithium and corresponding magnesium organo-compounds do not necessarily react in the same way,[7,8] but such differences are not a general feature of tin alkylation reactions.[9] In this study it has been found that the reaction of di-t-butyl(phenyl)tin(IV) chloride with both types of reagent gives the same coupled product, and the reaction of neophyl(diphenyl)tin(IV) iodide yields the identical substituted product as in equation (1). By contrast, reaction of neophyl(diphenyl)tin(IV) with an excess of t-pentylmagnesium chloride yielded only a dimerized product [equation (2)].

$$(Ph)_2[Ph(Me)_2CCH_2]SnI + Bu^tLi(MgX) \longrightarrow (Ph)_2[Ph(Me)_2CCH_2]Bu^tSn \tag{1}$$

$$(Ph)_2[Ph(Me)_2CCH_2]SnI + (MeCH_2CMe_2)MgCl \longrightarrow (Ph)_2[Ph(Me)_2CCH_2]Sn{-}Sn[Ph(Me)_2CCH_2](Ph)_2 \tag{2}$$

Other reactions of triorganotin(IV) iodide compounds with t-pentylmagnesium chloride are depicted in equations (3)—(6). Thus reactions (2)—(5) all yield a coupled

$$(Ph)_3SnI + (MeCH_2CMe_2)MgCl \longrightarrow (Ph)_3Sn{-}Sn(Ph)_3 \tag{3}$$

$$(Ph)_2Bu^tSnI + (MeCH_2CMe_2)MgCl \longrightarrow (Ph)_2Bu^tSn{-}SnBu^t(Ph)_2 \tag{4}$$

$$Ph(PhCH_2)Bu^tSnI + (MeCH_2CMe_2)MgCl \longrightarrow Ph(PhCH_2)Bu^tSn{-}SnBu^t(PhCH_2)Ph \tag{5}$$

$$(Ph)_2(PhCH_2)SnI + (MeCH_2CMe_2)MgCl \longrightarrow (Ph)_2(PhCH_2)(MeCH_2CMe_2)Sn \tag{6}$$

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[6] S. A. Kandil and A. L. Allred, *J. Chem. Soc.* (*A*), 1970, 83.

[7] S. A. Kandil and R. E. Dessy, *J. Amer. Chem. Soc.*, 1966, **88**, 3027.

[8] D. B. Chambers and F. Glockling, *J. Chem. Soc.* (*A*), 1968, 735.

[9] H. J. Gotze, *Chem. Ber.*, 1972, **105**, 1775.

product with no incorporation of the t-pentyl group. Reaction (6), like its t-butyl-lithium counterpart, gave a substituted product. The incorporation of the t-pentyl group thus appears to depend primarily on steric factors to an even greater degree than does the incorporation of a t-butyl group.

Anisochronous Effects.—Anisochronous behaviour of protons on a dissymmetric tin moiety appear to have been previously limited to compounds containing a neophyl group and, in most cases, containing a halide group also.[10] The effect of dissymmetry on $^2J_{\mathrm{SnH}}$ has also been noted in halide compounds.[11] We have examined a variety of triorganotin(IV) halide compounds containing a t-butyl group and two other different (but not neophyl) organic groups, at least one of which contained a diastereotopic pair of proton sites. In no case was magnetic non-equivalence observed in the 220 MHz n.m.r. spectrum. The diphenyl compound from reaction (6) was used to prepare the dissymmetric iodide compound of reaction (7). This has diastereotopically related benzylic protons and a diastereotopic pair of methyl groups in the t-pentyl radical. The former gave a single ^{1}H n.m.r. absorption, but the latter pair were anisochronous to the extent of 0·02 p.p.m. The lack of splitting for the benzylic protons can be misleading since these protons are geminal and spin-coupled. Their coupling constant of about 12 Hz requires a chemical-shift difference of more than 3 Hz before splitting can be observed at the usual resolution of 0·3 Hz. It is possible that the anisotropic effect of the tin–iodine bond is responsible for the magnetic non-equivalence, since on substitution of the iodide group by a fourth organic group the anisochronous effects disappear. These diastereotopic t-pentyl methyl groups provide an unusual example of anisochronous behaviour in the presence of a chiral tin atom which is not bearing a neophyl group.[4,10]

$$\mathrm{(Ph)_2(PhCH_2)(MeCH_2CMe_2)Sn + I_2 \longrightarrow Ph(PhCH_2)(MeCH_2CMe_2)SnI + PhI} \quad (7)$$

The Tetra-alkyl Compounds.—Dissymmetric tetra-alkyltin(IV) compounds exhibiting anisochronous behaviour in their n.m.r. spectra have been limited to those with a neophyl group. Previous work[4] has indicated that the phenyl ring of the neophyl group is responsible for the anisotropic shielding of benzylic protons attached to the same tin atom. Molecular models suggested that the neophyl group can fold back so that the phenyl ring could approach and influence the benzylic protons.

Using the benzyl(neophyl)(phenyl)tin(IV) moiety as a probe, a study was made of methyl, isopropyl, t-butyl, and t-pentyl compounds in which it should be increasingly difficult for the neophyl phenyl ring to approach the tin atom. The splitting of the benzylic protons was found to rapidly decrease from the methyl to the t-pentyl compound (Table), supporting the suggestion of Stynes and Allred[4] regarding the role of the neophyl group. However, at the same time, the neophyl methyl and methylene protons showed increased splitting from the methyl to the t-pentyl compound (Table). These neophyl protons must experience increasingly different shieldings from the neophyl phenyl ring as steric effects impose restraints on the orientation of the neophyl group itself. Both effects are consistent with the view[4] that the contribution to the splitting due to intrinsic asymmetry[12] is very small in these compounds.

Replacement of either the phenyl or benzyl group by a bulkier substituent should cause similar changes in the splittings. In the *isopropyl* compound of the benzyl(neophyl)(phenyl)tin(IV) moiety, the isopropyl methyl groups were anisochronous to a very small extent (2·0 Hz at 220 MHz). In the compound benzyl(t-butyl)(neophyl)(isopropyl)tin(IV), the splitting of the neophyl methyl, methylene, and isopropyl methyl protons were increased while that of the benzylic protons was decreased. In the compound t-butyl(neophyl)(phenyl)(isopropyl)tin(IV), the splittings of the relevant neophyl and isopropyl groups were similarly increased. Undoubtedly the anisotropic effects of both the phenyl and benzyl groups influence the net chemical shift of protons on other groups. However, neither seems to have an important effect on the appearance of diastereotopic non-equivalence.

The relevant data are listed in the Table. The splittings reported (Δ/p.p.m.) are the actual calculated chemical shifts, and will only be directly observable if the protons involved are not spin-coupled. In most cases it was necessary to resort to 220 MHz spectra to see all the splittings for any one compound. Stynes and Allred[4] have indicated that larger diastereotopic effects in their dissymmetric neophyltin compounds are associated with high-field shifts for methyl and benzylic protons, and with low-field shifts for the neophyl protons. In the present series, the trends are not so clear, although the presence of a neophyl group does in general appear to cause upfield shifts for the protons on other groups.

Exchange.—Enantiomer exchange has been noted for halogen dissymmetric tin compounds.[4,10] This leads to coalescence of the separate n.m.r. peaks of diastereotopically related protons and provides some information on the rate at which racemization is occurring. It has been observed that bases such as pyridine can catalyse this exchange, and the effect of such catalysts on the diastereotopic splitting of the compound benzyl(methyl)(neophyl)(phenyl)tin(IV) has been investigated previously.[4] Unfortunately, pyridine can induce an aromatic-solvent shift and the results presented were necessarily rather inconclusive.

In the present series, pyridine was added routinely to carbon tetrachloride solutions of the dissymmetric compounds. In no case was any effect observed other than small changes in chemical shifts. By contrast, addition of pyridine to solutions of the dissymmetric

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[12] M. Raban, *Tetrahedron Letters*, 1966, 3105.

iodide intermediate compounds always destroyed anisochronous behaviour. The major difference between coalescence of two or more resonances due to site exchange and apparent coalescence due to overlap of accidentally degenerate peaks is in the precoalescence behaviour. Exchange coalescence exhibits line broadening before any decrease in chemical-shift difference is observed.[5] Coalescence due to peak overlap, in the absence of exchange, does not require changes in relaxation times. Thus individual linewidths tend to remain constant and broadening effects only occur when chemical-shift differences approach the limit of resolution. With this in mind, the methyl, isopropyl, and t-butyl compounds of the benzyl(neophyl)(phenyl)tin(IV) moiety were examined over the temperature range of the solvent. Raising the temperature decreased the splittings (Δ) (Table) by *ca.* 0·01 p.p.m. per 30 °C. This alone is an indication that exchange is not responsible, since such a small change over 30 °C near ambient temperatures would yield activation energies much too small to allow observation of individual sites by n.m.r. without invoking abnormally large negative entropy contributions. In addition, this chemical-shift change was unaccompanied by any significant change in half-height linewidth of the resonances involved. It therefore seems reasonable to rule out inversion processes of the tetrasubstituted tin compounds, at least up to 60 °C, thus permitting, in principle, isolation of stable optically pure compounds.

Dissymmetric derivatives of tin

	Chemical shift, τ/p.p.m. ($10^2\Delta$/p.p.m.)[a]					Analysis (%)			
	Benzyl	Neophyl				C		H	
Compound	CH$_2$	CH$_2$	CH$_3$	Other[b]	n_D(t/°C)	Calc.	Found	Calc.	Found
Ph(PhCH$_2$)[Ph(Me)$_2$CCH$_2$](Me)Sn	7·82(11·2)	8·39(n)	8·66(0)	Me: 10·17	1·5958(20)	66·25	67·15	6·50	6·75
Ph(PhCH$_2$)[Ph(Me)$_2$CCH$_2$](Pr^i)Sn	7·80(8·9)	8·41(n)	8·67(0·6)	Pr^i: CH 8·82; CH$_3$ 9·00(0·9)	1·5917(20)	67·4	68·1	6·95	7·30
Ph(PhCH$_2$)[Ph(Me)$_2$CCH$_2$](Bu^t)Sn	7·81(3·5)	8·38(4·1)	8·66(1·7)	Bu^t: 9·02	1·5913(22)	67·95	68·45	7·20	7·00
Ph(PhCH$_2$)[Ph(Me)$_2$CCH$_2$](MeCH$_2$CMe$_2$)Sn	7·76(n)	8·38(5·2)	8·69(2·0)	MeCH$_2$CMe$_2$: α-CH$_3$ 9·01(0); α-CH$_2$ *ca.* 8·8; β-CH$_3$ 9·28	*c*				
Ph[Ph(Me)$_2$CCH$_2$](Bu^t)(Pr^i)Sn		8·32(3·5)	8·60(1·5)	Bu^t: 8·88 Pr^i: CH 8·58; CH$_3$ 8·83(1·3)	1·5558(20)	64·35	64·7	8·00	8·55
PhCH$_2$[Ph(Me)$_2$CCH$_2$](Bu^t)(Pr^i)Sn	8·01(4·5)	8·59(3·4)	8·65(2·2)	Bu^t: 9·01 Pr^i: CH 8·82; CH$_3$ 8·97(1·1)	1·5614(22)	65·05	64·9	8·20	8·15
Ph(PhCH$_2$)(Bu^t)(MeCH$_2$CMe$_2$)Sn	7·38(n)			Bu^t: 8·83 MeCH$_2$CMe$_2$: α-CH$_3$ 8·79(0); α-CH$_3$ 8·45; β-CH$_3$ 9·18	1·5651(24)	63·65	64·05	7·75	8·00
[Ph(PhCH$_2$)(Bu^t)Sn]$_2$	7·36(n)			Bu^t: 8·87	(m.p. 106—107)	59·35	59·3	6·10	6·05
(Ph)$_3$[Ph(Me)$_2$CCH$_2$]Sn		7·94	8·60		(m.p. 94—95)	69·75	69·45	5·80	5·55
[(Ph$_2$(Bu^t)Sn]$_2$				Bu^t: CH$_3$ 8·75	(m.p.) 131—132)	58·25	58·5	5·75	6·00
[(Ph)$_2${Ph(Me)$_2$CCH$_2$}Sn]$_2$		8·07	8·78		(m.p. 114—115)	65·05	64·95	5·65	5·60
(Ph)$_2$(PhCH$_2$)(MeCH$_2$CMe$_2$)Sn	7·22			MeCH$_2$CMe$_2$: α-CH$_3$ 8·77; α-CH$_2$ 8·46; β-CH$_3$ 9·14	1·6096	66·25	66·6	6·50	6·20
(Ph)$_2$(PhCH$_2$)(Bu^t)Sn	7·30			Bu^t: CH$_3$ 8·84	1·6049(24)	65·6	65·75	6·20	6·15
(Ph)$_2$(PhCH$_2$)[Ph(Me)$_2$CCH$_2$]Sn	7·70	8·24	8·70		1·6225(24)	70·05	70·15	6·10	6·20
(Ph)$_2$[Ph(Me)$_2$CCH$_2$](Me)Sn		8·16	8·64	MeCH$_3$: 9·88	1·5990(24)	65·6	65·4	6·20	6·40
(Ph)$_2$[Ph(Me)$_2$CCH$_2$](Pr^i)Sn		8·15	8·62	Pr^i: CH 8·6; CH$_3$ 8·85	1·5948(22)	66·85	66·55	6·75	6·55
(Ph)$_2$[Ph(Me)$_2$CCH$_2$](Bu^t)Sn		8·11	8·64	Bu^t: CH$_3$ 8·85	1·5846(24)	67·4	66·7	6·95	7·25

[a] Chemical-shift difference of diastereotopic protons: $10^2\Delta$ = chemical shift (Hz) at 100 MHz; n = no splitting observed at 220 MHz for AB system. [b] Phenyl region *ca.* 6·7—7·3 for all compounds. [c] Contaminated with dineophyl.

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