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HOMOLYTIC ORGANOMETALLIC REACTIONS

XII *. HOMOLYTIC DEALKYLATION OF DI-n-BUTYL-t-BUTYLTIN CHLORIDE: PREFERENTIAL DISPLACEMENT OF THE n-BUTYL RADICAL

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Summary

t-Butoxyl radicals react with di-n-butyl-t-butyltin chloride to show the ESR spectrum of the n-butyl rather than the t-butyl radical. Cumyloxyl radicals behave similarly, but trimethylsiloxyl and benzoyloxyl radicals react to give both n-butyl and t-butyl radicals. The unexpected preferential formation of the less stable n-alkyl radical is tentatively ascribed to steric constraints in a 5-coordinate intermediate.

It is normally observed that the ease of formation of primary, secondary and tertiary alkyl radicals follows the sequence p-R < s-R < t-R. Exceptions to this rule have attracted much attention **, and investigations into their cause *** have often contributed to our understanding of the way in which polar and steric effects control homolytic reactivity.

We report here that the S_H2 reactions of a number of oxygen-centered radicals at the tin atom in di-n-butyl-t-butyltin chloride provide a new exception to this rule in that the n-butyl radical is often displaced in preference to the t-butyl radical (eq. 1).

$$RO\cdot + n\text{-}Bu_2\text{-}t\text{-}BuSnCl \rightarrow ROSn\text{-}n\text{-}Bu\text{-}t\text{-}BuCl + n\text{-}Bu\cdot \quad (1)$$

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* Part XII see Ref. 1.

** e.g. The ring-opening of ring-substituted cyclopropylmethyl radicals [2].

*** e.g. The ring-closure of 5-hexenyl radicals [3].

Experimental

Preparation of di-n-butyl-t-butyltin chloride

A solution of t-butylmagnesium chloride (from t-butyl chloride (9.3 g, 0.1 mol) and magnesium (2.4 g, 0.1 mol)) in ether (100 ml) was added to di-n-butyltin dichloride (30 g, 0.1 mol) in ether (200 ml) during 1 h. The product was hydrolysed with aqueous ammonium chloride (15 g), and the ethereal layer was separated and treated with a solution of potassium hydroxide (8 g) in water (50 ml) when dibutyltin oxide separated as a white solid. The ether layer was separated, treated with 4 *N* HCl (10 ml), washed with water and dried ($MgSO_4$). Distillation gave n-Bu_2-t-BuSnCl (4.0 g), b.p. 82—83° C/0.15 mmHg. Found: C, 44.4; H, 8.3; Cl, 10.7. $C_4H_{27}ClSn$ calcd.: C, 44.3; H, 8.4; Cl, 10.9%. ^1H NMR τ 8.78 (s, t-Bu), 8.33—9.09 (n-Bu). ^{13}C NMR δ 15.5 (α-CH_2), 28.3 (β-CH_2), 27.2 (γ-CH_2), 13.6 (δ-CH_3), 31.5 ($\underline{C}Me_3$), 29.4 ($C\underline{Me}_3$). Kandil and Allred [4] report b.p. 82—84°C/4 mmHg, ^1H NMR τ 8.83 (t-Bu).

In the ^{13}C NMR spectrum, any signals due to di-n-butyltin dichloride (δ 27.0, 26.3, 26.0, and 13.5) or of tri-n-butyltin chloride (δ 28.1, 27.0, 17.6, and 13.6) were below the noise level, and the concentration of these impurities, if present, were judged to be less than about 2%.

The di-n-butyl-t-butyltin chloride, tri-n-butyltin chloride, and di-n-butyltin dichloride were subjected to gas-liquid chromatographic analysis on a Varian Aerograph 920 instrument fitted with a 12′ × 3/16″ column of Fluorosilicone Oil FS1265 (QF.1) and Katharometer detector. With helium (0.92 ml s^{-1}) as the carrier gas, and at 170° C, retention times were as follows: n-Bu_2SnCl_2 1770 s, n-Bu_3SnCl, 1770 s, n-Bu_2-t-BuSnCl 1290 s.

A solution of n-Bu_2-t-BuSnCl and di-t-butyl peroxide in cyclopropane was photolysed in the spectrometer cavity for 30 min, then the tube was opened at low temperature and the volatile material allowed to evaporate. The original and the residual organotin compound were analysed by gas liquid chromatography, and both showed the absence of Bu_2SnCl_2 and of Bu_3SnCl down to limit of detection (ca. 1%).

ESR experiments

A solution of the appropriate organic peroxide (di-t-butyl peroxide, dicumyl peroxide, bis(trimethylsilyl) peroxide, or benzoyl peroxide), and the organotin compound in cyclopropane (or toluene for benzoyl peroxide) was photolysed in the cavity of a Varian E4 spectrometer by the technique which has been described, and the spectra of the radicals which were formed were recorded over a range of temperature [5].

The rate constants for the S_H2 reactions were determined by causing triisobutylborane to compete with the organotin compound for reaction with the peroxide-derived radicals, and comparing the intensities of the n-butyl and isobutyl radicals which were formed [5].

Results

Di-n-butyl-t-butyltin chloride was prepared by Kandil and Allred [4] as a yellow oil from the reaction between di-n-butyltin dichloride and t-butyllithium.

We used instead the reaction of t-butylmagnesium chloride with di-n-butyltin dichloride, and obtained the product as a colourless oil, but with physical properties otherwise similar to those which had been reported, and with a satisfactory analysis.

We have shown previously that tri-n-butyltin chloride and di-n-butyltin dichloride (though not tetra-n-butyltin or n-butyltin trichloride) will undergo alkoxydealkylation to give ESR spectra of the n-butyl radical [6], and it was therefore important to establish the absence of these compounds in our sample of di-n-butyl-t-butyltin chloride. Proton NMR was not capable of doing this because of the complex pattern of signals due to the n-butyl group, but ^{13}C-NMR spectroscopy can distinguish between n-Bu_2-t-BuSnCl, Bu_3SnCl, and Bu_2SnCl_2 in mixtures, and showed our sample was free from tri-n-butyltin chloride and di-n-butyltin dichloride down to the limit (ca. 2%) imposed by the noise level of the spectra. Gas liquid chromatography can also readily distinguish between n-Bu_2-t-BuSnCl, n-Bu_3SnCl, and n-Bu_2SnCl_2, and again neither contaminant could be detected (≯ca. 1%) by this technique, either in the freshly prepared material, or after it had been irradiated with UV light in the presence of di-t-butyl peroxide.

A solution of di-t-butyl peroxide and di-n-butyl-t-butyltin chloride in cyclopropane was photolysed in an ESR cavity and immediately gave rise to a strong spectrum of the n-butyl radical (eq. 1, R = t-Bu; see Fig. 1), which persisted for as long as the photolysis was continued (ca. 1 h) *. The positions where the six strongest lines of the t-butyl radical should appear are indicated on Fig. 1, and weak signals of the two inner lines can just be detected; the intensity of these signals relative to those of the n-butyl radical did not change significantly over

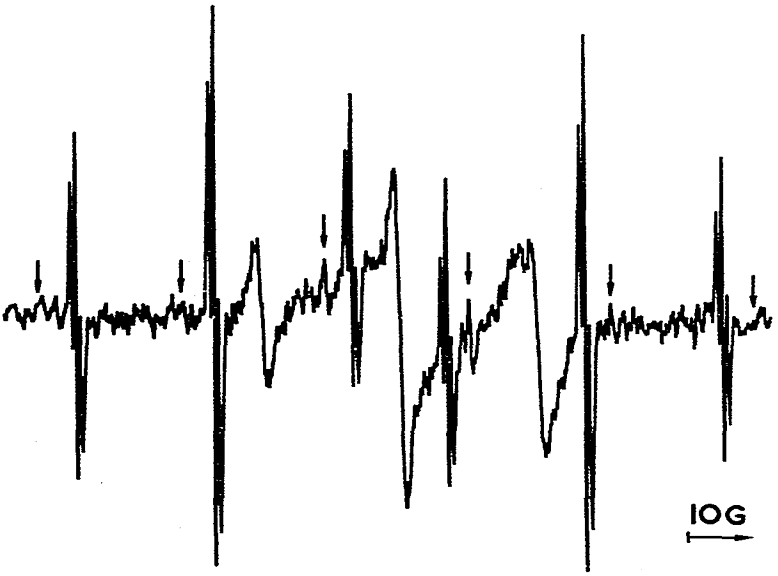

Fig. 1. ESR spectrum of the n-butyl radical obtained from the photolysis of di-t-butyl peroxide in the presence of di-n-butyl-t-butyltin chloride in cyclopropane at −120°C.

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* No spectrum was observed in the absence of the peroxide.

TABLE 1

RATE CONSTANTS FOR t-BUTOXYDE-n-BUTYLATION IN CYCLOPROPANE

	k (l mol^{-1} s^{-1}) at —60°C
n-Bu$_2$t-BuSnCl	4.5×10^5
n-Bu$_3$SnCl	2.1×10^6
n-Bu$_2$SnCl$_2$	3.0×10^6

the temperature range —50 to —150° C, or during the period of the photolysis. The distortion of the line with $M_{I\alpha}$ + 1, $M_{I\beta}$ 0 in the spectrum of the n-butyl radical is due to the gradual development of a strong broad singlet with a *g*-factor of about 1.9905 which is commonly observed during photolytic reactions with organotin compounds, and which may be associated with an $\cdot SnX_5$ species.

Similar spectra were obtained using samples of di-n-butyl-t-butyltin chloride from two other independent preparations.

Similar experiments were carried out with dicumyl peroxide, bis(trimethylsilyl) peroxide [7], and benzoyl peroxide (the last in toluene solvent), as the photolytic source of oxyl radicals. The reaction of the cumyloxyl radicals was similar to that of the t-butoxyl radicals: the spectrum which was observed over the temperature range —60 to —120° C was overwhelmingly that of the n-butyl radical, with the t-butyl radical being just detectable.

Trimethylsiloxyl radicals [8] reacted less selectively, and the spectra of both the n-butyl and t-butyl radicals were apparent in the relative concentrations of about 3.0 : 1 at —100° C, and 2.5 : 1 at —10° C.

In toluene at low temperatures, benzoyl peroxide acts as a photolytic source of benzoyloxyl radicals. Under these conditions, tri-n-butyltin chloride shows a strong spectrum of the n-butyl radical, but di-n-butyl-t-butyltin chloride at —60° C gave a weak spectrum which was principally that of the t-butyl radical, with some indication of the presence also of the n-butyl radical.

The rate constants for the t-butoxyde-n-butylation of di-n-butyl-t-butyltin chloride, tri-n-butyltin chloride, and di-n-butyltin dichloride in cyclopropane were determined by the ESR technique, and the results are given in Table 1.

Discussion

It is vital to establish that the n-butyl radicals which are observed are not formed by the dealkylation of tri-n-butyltin chloride or of di-n-butyltin dichloride which might arise from the disproportionation of di-n-butyl-t-butyltin chloride, or from some other source. For the following reasons, we discount this possibility.

(1) The concentrations of these impurities, if present, in the di-n-butyl-t-butyltin chloride as it was introduced into the ESR tube or after it had been irradiated briefly in the presence of di-t-butyl peroxide, were below the limits which we could detect by ^{13}C NMR or, more particularly, by GLC.

(2) The intensity of the ESR spectrum of n-Bu· did not change substantially during the period of photolysis. This would not be compatible with the reaction of a small amount of initial impurity which would rapidly be consumed, or with

the photo-induced formation of an impurity which would have a zero initial concentration, and should give a very weak spectrum in the early stages of the photolysis.

(3) The relative reactivities of the organotin compounds are such (Table 1) that a substantial amount of tri-n-butyltin chloride or of di-n-butyltin dichloride (20% and 13% respectively) would need to be present in the di-n-butyl-t-butyltin chloride to give the rate of production of n-butyl radicals which is observed, and these concentrations would easily have been detected by GLC and ^{13}C NMR.

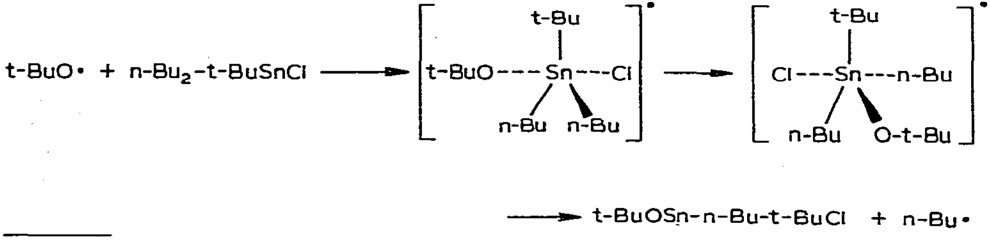
We conclude that di-n-butyl-t-butyltin chloride does react with t-butoxyl radicals to give the less thermodynamically stable n-butyl radical rather than the t-butyl radical. We have shown previously that the relative reactivities of different trialkylboranes, R_3B, towards ROO• [9], t-BuO• [10], or BuS• [11] radicals *, or acetone triplets [13], and of different tetra-alkyltins towards $(CH_2CO)_2N$• radicals [14] is reduced as the bulk of the alkyl groups increases, and the five fold decrease in reactivity towards t-BuO• radicals which we observe in going from tri-n-butyltin chloride to di-n-butyl-t-butyltin chloride fits in with this picture of steric control of reactivity.

No more than a tentative suggestion can be made as to why the different oxyl radicals react with different selectivities, and why, in particular, t-butoxyl and cumyloxyl radicals displace the less stable n-butyl radical.

There is some evidence that the homolytic displacement at tin proceeds through the formation of a 5-coordinate intermediate rather than transition state [6,15, 16], and Symons has suggested [17] that the species •SnX_5 with 9 valence electrons has the structure of a trigonal bipyramid with three strongly bound equatorial groups, two weakly bound apical groups sharing two electrons in a three-centre bond, and the odd electron in an almost non-bonding orbital on the two apical groups.

Such a radical might be expected to have properties similar to those of the phosphoranyl (•PX_4) radical [18]: the most stable configuration will be that in which the most electronegative groups occupy apical sites, but the several ligands can exchange their positions, and loss of an alkyl group will occur preferentially from the apical position.

Such an apical site has three other ligands at 90°, whereas an equatorial site has only two ligands at 90°. If, as the rate constants for the S_H2 process imply, the reactivity is limited by steric factors, the bulky t-butyl group will prefer to occupy a less-congested equatorial site, placing a n-butyl group in the apical (leaving) position. The process shown in eq. 2 would then be compatible with our observations.



(2)

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* In the reaction of RO•, RS•, or ROO• radicals with mixed trialkylboranes, the ease of displacement of the various groups follows the normal sequence t-R > s-R > p-R [12].

The significance of our result with benzoyloxyl radicals is questionable because the spectra were weak, but a different selectivity might be connected with the fact that the acyloxyl group on tin can act as a chelating ligand [19] rendering the intermediate not trigonal bipyramidal but octahedral, in which structure the above argument would not apply.

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