

## Preliminary communication

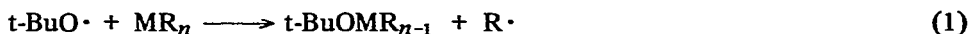
### Bimolecular homolytic alkoxydealkylation of organotin compounds

ALWYN G. DAVIES, B.P. ROBERTS and J.C. SCAIANO

Chemistry Department, University College London, 20 Gordon Street, London WC1H 0AJ  
(Great Britain)

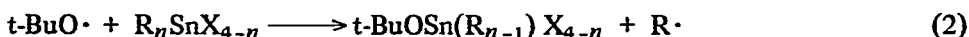
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Alkoxydealkylation of organometallic compounds according to equation (1) has been demonstrated for derivatives of metals of the Main Groups I, II, III and V<sup>1,2</sup>, but not before, unambiguously, of Group IV.



Thus, if di-*t*-butyl peroxide is photolysed in the presence of tetraethyltin at  $-9^\circ$  in the cavity of an ESR spectrometer, the spectrum of the radical  $\text{Et}_3\text{Sn}\dot{\text{C}}\text{HCH}_3$  [ $a(\text{CH})$  20.1G,  $a(\text{CH}_3)$  25.6G]<sup>★</sup>, and not of the ethyl radical, is observed. Similarly, at  $-50^\circ$ , tributyltin propoxide under the same conditions shows the spectrum of only the radical  $\text{Bu}_3\text{SnO}\dot{\text{C}}\text{HCH}_2\text{CH}_3$  [ $a(\text{CH})$  13.2G,  $a(\text{CH}_2)$  20.6G].

We now report that the presence of suitable electronegative ligands at the tin centre in the compounds  $\text{R}_n\text{SnX}_{4-n}$  ( $n = 1-3$ ) greatly increases the rate of attack at tin relative to that at hydrogen, and homolytic substitution at the metal centre can be observed (eqn. 2).



For example, when di-*t*-butyl peroxide is photolysed in the presence of the alkyltin chlorides,  $\text{R}_n\text{SnCl}_{4-n}$ , ( $\text{R} = \text{Et}, \text{Pr}$  or  $\text{Bu}$ ;  $n = 3$  or  $2$ ) in toluene, cyclopentane or benzene, excellent spectra of the appropriate radical,  $\text{R}\cdot$ , are observed<sup>★★</sup>. Under the same conditions, 1,1,3,3-tetrabutyl-1,3-dichlorodistannoxane and alkyltin carboxylates (e.g.  $\text{Et}_3\text{SnO}\cdot\text{CO}\cdot\text{H}$ ,  $\text{Pr}_3\text{Sn}\cdot\text{O}\cdot\text{CO}\cdot\text{Me}$ , and  $\text{Pr}_3\text{Sn}\cdot\text{O}\cdot\text{CO}\cdot\text{CF}_3$ ) similarly show the spectrum of the appropriate radical  $\text{R}\cdot$ .

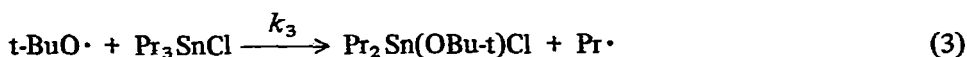
Organotin halides and carboxylates which had been subjected to prolonged

★ Krusic and Kochi<sup>3</sup> report that at  $-104^\circ$ ,  $a(\text{CH})$  20.41G and  $a(\text{CH}_3)$  25.89G, and the spectrum of the radical  $\text{Et}_3\text{SnCH}_2\dot{\text{C}}\text{H}_2$  can also be detected.

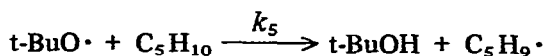
★★ In the absence of the peroxide the intensity of the spectra are reduced by 80–85% corresponding to a 25-fold reduction in the rate of production of radicals.

irradiation in the presence of the peroxide, or which had not been recently purified, gave a broad singlet,  $g = \text{ca. } 1.99$ , as well as the multiplet of the radical  $R\cdot$ , but the kinetics of the alkoxydealkylation (see below) were unchanged, and experiments at varying light intensities showed that this singlet did not represent a species on the reaction coordinate. It is possible that it may be associated with a tin-centred radical.

Reaction (2) also occurs as one component of a chain process when compounds  $R_n\text{SnX}_{4-n}$  are treated with *t*-butyl hypochlorite. For example, tripropyltin chloride reacts vigorously with *t*-butyl hypochlorite in carbon tetrachloride at room temperature to give propyl chloride (NMR and GLC; ca. 70% yield) and dipropyltin-*t*-butoxide chloride (identified by its reaction with bipyridyl to give  $\text{Pr}_2\text{SnCl}_2 \cdot \text{bipy}$ ). The reaction could be inhibited completely by galvinoxyl.



If cyclopentane is caused to compete (eqn. 5) with the tripropyltin chloride for reaction with the *t*-butoxy radicals, the relative concentrations of the propyl and cyclopentyl radicals can be monitored by ESR, and the relative values of the second order rate constants  $k_3$  and  $k_5$  can be derived<sup>4</sup>.



These give a good Arrhenius plot over the range  $-92^\circ$  to  $+15^\circ$  of the form

$$\log k_3/k_5 = (-2.12 \pm 0.20) + (4.050 \pm 0.204) / \theta$$

where  $\theta = 2.303RT \text{ kcal}\cdot\text{mol}^{-1}$ ,

$$\text{whence } k_3 = 10^{6.88} \cdot e^{-1.130/\theta} \text{ l}\cdot\text{mol}^{-1}\cdot\text{sec}^{-1}$$

$$\text{and } k_3(30^\circ) = 1.1 \cdot 10^6 \text{ l}\cdot\text{mol}^{-1}\cdot\text{sec}^{-1}$$

For comparison, the rate constant for *t*-butoxydealkylation of tri-*n*-butylborane at  $30^\circ$  is about  $1 \cdot 10^7 \text{ l}\cdot\text{mol}^{-1}\cdot\text{sec}^{-1}$  (ref. 5).

Photoexcited ketones (e.g.  ${}^3n \longrightarrow \pi^*$  acetophenone and  ${}^3\pi \longrightarrow \pi^*$  *p*-methylacetophenone) similarly displace an alkyl radical from tin in organotin halides<sup>6</sup>, and it seems likely that many other radical reagents will behave in the same way. This extension of the  $S_H2$  mechanism of dealkylation to the Group IV metals<sup>\*</sup> has important theoretical and practical implications. It opens up the possibility of studying the steric course of the reaction, and suggests a new interpretation of the mode of action of organotin compounds in some industrial applications.

\* There appears to be still no simple example of an  $S_H2$  reaction at saturated carbon.

## REFERENCES

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- 3 P.J. Krusic and J.K. Kochi, *J. Amer. Chem. Soc.*, 91 (1969) 6161.
- 4 cf. A.G. Davies, D. Griller and B.P. Roberts, *J. Chem. Soc. B*, (1971) 1823.
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- 6 cf. A.G. Davies, B.P. Roberts and J.C. Scaiano, *J. Chem. Soc. B*, (1971) 2171.

*J. Organometal. Chem.*, 39 (1972)