

Intramolecular Nucleophilic Assistance at Tin: Reversal of Selectivity in S_E2 Cleavage of Mixed Tetraorganotin Compounds by Iodine

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Electrophilic cleavage of mixed-functionality tetraorganotin compounds by iodine reveals a complete reversal of the usually observed selectivity, *i.e.* alkyltin-carbon bonds are broken in preference to aryl- or vinyl-tin-carbon bonds; this unexpected result is explained by intramolecular assistance at tin.

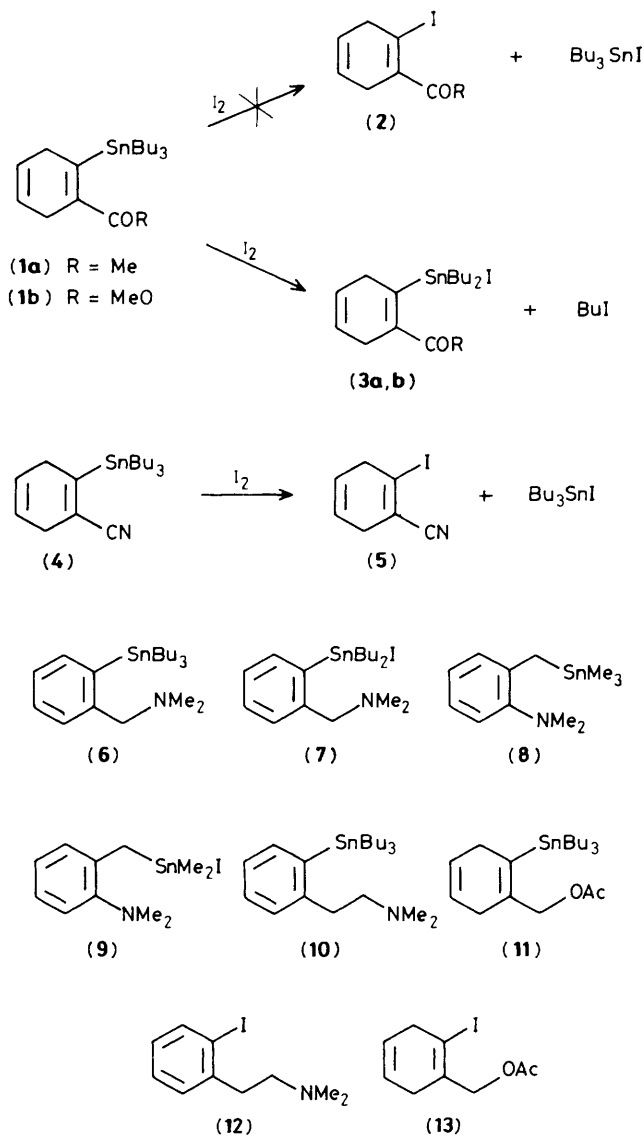
A considerable amount of data on electrophilic cleavage of metal-carbon bonds concerning mercury and group 4B metal derivatives is now available.¹ These studies have been developed primarily because the very high selectivity of electrophilic demetallation provides useful synthetic applications.² The ease of cleavage by halogens of mixed organotin derivatives follows the sequence benzyl > aryl \approx vinyl > methyl > higher alkyl.³ For mixed tetra-alkyltin compounds, a cyclic or an open S_E2 transition state^{4,5} or a charge-transfer mechanism⁶ has been proposed to account for selectivity, solvent effects, and configurational changes at the cleaved organic group, whereas an open S_E2 transition state with assistance from the solvent or another molecule of electrophile is the generally accepted mechanism for aryl- or vinyl-tin derivatives.⁷

We report here the first examples of halogenodemetallation where the usual sequence of reactivity is reversed, *i.e.* where alkyl groups are cleaved preferentially to aryl, vinyl, or benzyl groups in mixed tetraorganotin derivatives, and propose an

interpretation of these unexpected results. In the course of our studies concerning vinyltin adducts obtained by Diels-Alder reaction of alkynyltin derivatives,⁸ we needed to prepare the corresponding iodides from (1) and iodine. But this anticipated facile reaction did not provide the desired product (2). †

Instead (3) resulting from the cleavage of a butyl-tin bond was recovered. As electronic effects of the substituent would

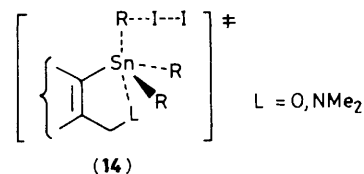
† Iododemetallation was carried out in $CDCl_3$ or C_6D_6 , in the dark, and followed using 1H n.m.r. spectroscopy. Compounds (3), (5), (7), (9), (11), (12), and (13) have been fully characterized by 1H n.m.r., mass, and i.r. spectroscopy, and (3), (7), and (9) by ^{119}Sn n.m.r. spectroscopy also. Compounds (3), (7), and (9) show an upfield shift of *ca.* 50 p.p.m. with respect to unco-ordinated halide, indicating strong chelation.⁹ Selectivity is at least 99% as checked by ^{119}Sn n.m.r. spectroscopy. Isolated yields of pure (3), (5), (7), (9), (12), and (13) are above 80%. We did not observe any solvent effect; the same results are obtained in non-polar (CCl_4 , $CHCl_3$, C_6H_6) or polar (MeOH) media. Added pyridine (10 equiv.) or radical inhibitor has no effect on the selectivity or on the course of the reaction.



destabilise the proposed open S_E2 transition state¹⁰ of this reaction, (4) was treated with iodine to give (5), indicating that the hypothesis of electronic effects¹¹ to explain the course of the reaction was not valid.

To find out if intramolecular chelation^{12‡} during the course of the reaction was the cause of the differences in reactivity between (1) and (4), amine (6), where intramolecular chelation is possible by formation of a five-membered ring,¹⁴ was treated with iodine. A 100% cleavage of a tin–butyl bond was observed giving (7). We extended this study to a benzylic derivative (8):¹⁵ a 100% cleavage of a tin–alkyl bond giving (9) occurs. With (10) and (11), where chelation is possible through a six- or seven-membered ring but less strong than in (6),^{16,17} the cleavage giving (12) or (13) is in agreement with

‡ ¹¹⁹Sn N.m.r. data show no evidence of chelation in our tetraorganotin derivatives. ¹¹⁹Sn N.m.r. (C_6D_6): –55.6 (3a), –57.7 (3b), –50.9 (6), –0.78 (8), –40.8 (10), –50.7 (11). Examples of internal co-ordination in tetraorganotin compounds have been only reported in one case where a nitrogen atom is linked to the tin by two or three carbon chains.¹³



the normal selectivity sequence: the aryl group is cleaved preferentially to the alkyl one. To account for these unexpected results we suggest an explanation based on geometrical arguments. Intramolecular assistance at tin by oxygen (1a,b) or nitrogen (6,8) during the approach of iodine to carbon can occur at an apical position, which is favoured for such an electronegative group. This co-ordination (which does not exist in the ground state)[‡] constrains the vinyl [in (1)], aryl [in (6)], or benzyl [in (8)] carbon linked to the tin to be in the equatorial position and the carbon of an alkyl group to be in an apical position.

Thus, the alkyl group becomes susceptible to electrophilic attack, see transition state (14). The alkyl–tin bond will be cleaved preferentially which explains the observed selectivity. In (10) or (11) the weaker co-ordination^{16,17} does not allow the reaction to follow the same pathway.

A similar rationalization has recently been proposed to explain the regioselective bromodemetalation of substituted tetra-alkyltins.¹⁸

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