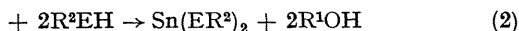
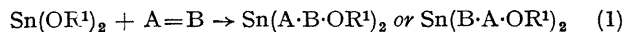


Addition and Substitution Reactions of Tin(II) Dimethoxide

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REACTIONS involving addition of M-ER systems (E = O, S, N, P, *etc.*) to multiple bonds are well known in tin(IV) systems,¹ where, for example, organotin(IV) alkoxides add to isocyanates to give *N*-stannylcarbamates.² We report the behaviour of the analogous tin(II) dimethoxide, which can be summarized in three general equations:



for which we present examples. Tin(II) dimethoxide was prepared by the method of Haendler, *et al.*,³ and used immediately.

Phenyl isocyanate undergoes a highly exothermic reaction with Sn(OMe)₂ in petrol to give in virtually quantitative yield a white solid whose i.r. spectrum exhibits strong absorptions at 1730 [ν(C=O)], 1070 and 1083 cm.⁻¹ [ν(C-O)]. Hydrolysis gave methyl *N*-phenylcarbamate, consistent with the formulation of the product as bis(methyl *N*-phenylcarbamate)tin(II), m.p. (sealed tube) 109–114°. The ^{119m}Sn Mössbauer spectrum, run immediately, exhibited a doublet with isomer shift consistent with the formulation as tin(II).⁴ Phenyl isothiocyanate was allowed to react slowly with Sn(OMe)₂ at room temperature to give an oil whose i.r. spectrum contained a strong absorption at 1140 cm.⁻¹, which can be assigned to ν(C=S) in a more unambiguous manner. In addition, the ready hydrolysis of the product to form

methyl *N*-phenylthiocarbamate can be taken as evidence for N-Sn rather than S-Sn bonding by analogy with the relative hydrolytic sensitivities of the tin(IV) systems.^{2,5} Chloral reacted exothermically with Sn(OMe)₂ to produce in virtually quantitative yield the crystalline tin(II) acetal, Sn[OCH(CCl₃)OMe]₂, m.p. (sealed tube) 73–74°, whose i.r. spectrum contained very strong, broad absorptions at 1080 and 830 cm.⁻¹ which can be assigned to ν(C-O) and ν(C-Cl) respectively. The Mössbauer spectrum confirmed the presence of tin as tin(II), but the hydrolysis product showed a ν(O-H) absorption at 3390 cm.⁻¹ and Mössbauer spectroscopy showed that the tin had been oxidised to Sn^{IV}.

Thiophenol reacted with Sn(OMe)₂ in benzene according to equation (2) with no evolution of heat. The pale yellow solid, m.p. 158–160° with darkening, formed in virtually quantitative yield, exhibited a doublet Mössbauer spectrum consistent with tin as tin(II), but a resonance in the tin(IV) region slowly appeared. Tin(II) dithiophenoxide takes up thiophenol in refluxing benzene after ½ hr., or on standing in air for 2 days, to give tin(IV) tetrathiophenoxide which is also produced directly from tin(II) dimethoxide and thiophenol in the presence of triethylamine.

Benzoyl chloride reacted with Sn(OMe)₂ according to equation (3) in an exothermic reaction to give tin(II) chloride and methyl benzoate in 82% yield.

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