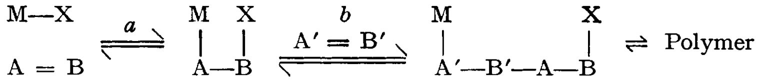
Trimerization of Isocyanates by Organotin Compounds

By A. J. BLOODWORTH and ALWYN G. DAVIES
(*William Ramsay and Ralph Forster Laboratories, University College, London, W.C.*1)

A LARGE group of reactions follows the general pattern shown in equation 1*a*, in which a metallic compound M–X (M = *e.g.* Sn, Si, Hg, Al, Mg; X = *e.g.* OR, OM, NR_2) adds to a multiple bond A=B, often reversibly.[1,2]

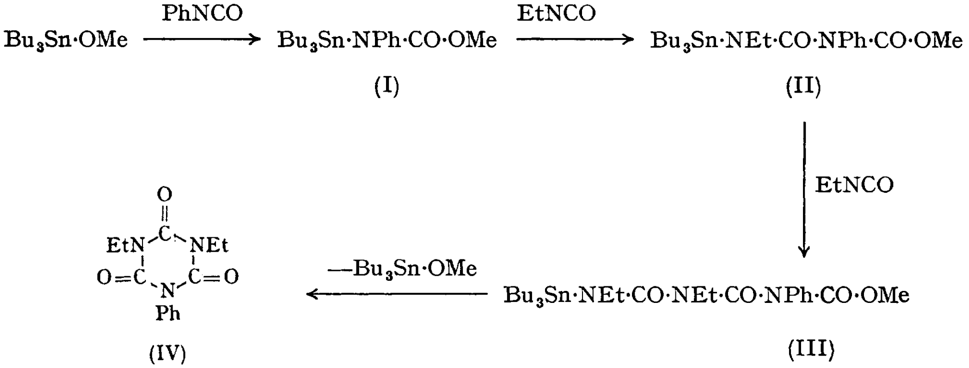
The new bond M–A may show a similar reactivity to the original bond M–X (particularly when A = O or RN); further units of the same or a different acceptor may then insert between M and A (eqn. 1*b*), building up an oligomer or polymer. This and the following communication report examples of this process where the initial addendum is a tin oxide or alkoxide, and the acceptor is an isocyanate or aldehyde, respectively.



(1)

Trialkyltin alkoxides and bis(trialkyltin) oxides will add to isocyanates to give isolable *N*-trialkyltincarbamates.[3] If these are treated with more of the isocyanate, the corresponding cyclic trimer, the isocyanurate, is formed. By this process we have isolated triethyl isocyanurate, triphenyl isocyanurate, and tri-1-naphthyl isocyanurate; this last compound, which is apparently not accessible by any of the other known routes to isocyanurates, has the high m.p. of 340°.

By the successive reaction of different isocyanates, a co-trimer can be built up. For example, if methyl *N*-tributylstannyl-*N*-phenylcarbamate (I), formed from tributyltin methoxide and phenyl



(2)

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[1] Bloodworth and Davies, *Proc. Chem. Soc.*, 1963, 315.
[2] Davies, *Trans. New York Acad. Sci.*, 1964, **26**, 923.
[3] Bloodworth and Davies, *Proc. Chem. Soc.*, 1963, 264.

isocyanate, is treated with ethyl isocyanate, diethyl phenyl isocyanurate (IV; m.p. 95—97·5°) is formed, *via*, we believe, the intermediate oligomers (II) and (III). By analogous reactions, ethyl diphenyl isocyanurate, m.p. 157—159°, and ethyl di-1-naphthyl isocyanurate, m.p. 202—204°, can similarly be prepared.

The fact that the trimerization apparently occurs across the N=C double bond might be taken to support our formulation of compound (I) as an N=C rather than a C=O adduct (*i.e.* $PhN{=}C(OMe){\cdot}O{\cdot}SnBu_3$). It seems probable, however, that isomers of these types are readily interconvertible, and that chemical reactions may be a poor criterion of structure.

The trimers reported here have been characterized by satisfactory analytical and molecular weight data, and, where appropriate, by integrated n.m.r. spectra.

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