Organometallic Diazoalkanes

By M. F. LAPPERT* and J. LORBERTH

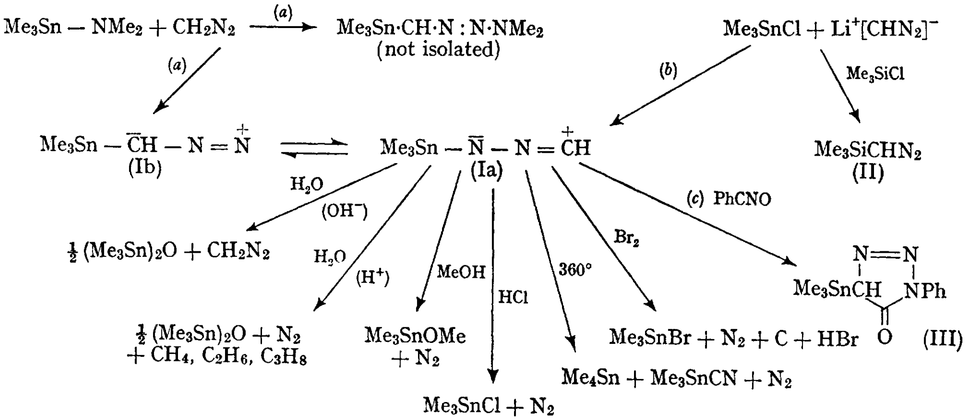
(*The Chemical Laboratory, University of Sussex, Brighton*)

WE report the first covalent organometallic diazoalkanes, Me_3SnCHN_2 (I, b.p. 64—67°/ 0·1 mm.) and Me_3SiCHN_2 (II, b.p. 80—85°/ 760 mm.), which are highly reactive compounds (see the Scheme).

The synthesis of (I) from diazomethane (reaction *a*) is visualized as an organometallic 1,3-dipolar insertion; such processes are novel in this area of chemistry.[1] An alternative mechanism[2] involves the assumption (for which there is some evidence[3]) that diazomethane behaves as a protic acid. Although diazomethane reacts as a 1,3-dipole, $\overset{-}{C}H_2—\overset{+}{N}=N$, with respect to alkenes and alkynes,[4] its previously studied reactions with organometallic compounds have led to methylene insertion or polymethylene with nitrogen loss (*e.g.*, for boron compounds, see ref. 5).

Compounds (I) and (II) are also conveniently obtained (reaction *b*) from the salt,[3] Li$^+$[CHN$_2$]$^-$. This route is perhaps of wider generality for extending the study of compounds having CHN$_2$$^-$ as a ligand.

The molecular weight of (I) in benzene, measured both cryoscopically and isopiestically, was strongly concentration dependent, with the degree of association between 1 and 2. The isodiazomethane (nitrile imine) structure (Ia) (shown for one canonical form) is preferred over the tautomeric diazomethane form (Ib) on the basis of the ^{1}H n.m.r. spectrum. This shows only protons associated with the Me$_3$Sn group [singlet at τ 9·53, with J(^{119}Sn–Me) = 57 and J(^{117}Sn–Me) = 54]; (*cf.*, diazomethane protons[6] at τ 6·92). The presence in the i.r. spectrum of a strong band at 2080 cm.$^{-1}$ (*cf.*, 2088 cm.$^{-1}$ in ethereal diazomethane[7]) is consistent with either structure (but not with the isomeric aziridine), as are the SnC$_3$ stretching modes at 530 and 488 cm.$^{-1}$. A weak absorption at 3240 cm.$^{-1}$ may arise from NH stretching (*cf.*, band at 3250 cm.$^{-1}$ in gaseous CH$_2$N$_2$, which is attributable[8] to the same mode). The u.v. spectrum had λ_{max} at 280vs and 396m mμ (*cf.*, diazomethane has four maxima[9] in the range 300–400 mμ). The mass spectrum of (I) did not reveal the parent molecular ion, but other features indicated the formation of (Me$_3$Sn)$_2$ in the electron beam.



Reaction *c* is noteworthy and may be capable of wide extension to other 1,3-dipolarophiles, to provide organometallic heterocycles such as the triazolone (III). This is a crystalline solid, m.p. 81—84° (decomp., with loss of N$_2$); the ^{1}H n.m.r. spectrum [Me$_3$Sn at τ 9·3, CH (?) at τ 8·8, and Ph centred at τ 2·6] indicates that its formation is best represented as 1,3-dipolar addition to (Ib). It is interesting that, by contrast, diazomethane reacts with phenyl isocyanate to provide nitrogen and the β-lactam of *N*-phenyl-β-alanine.[10]

(*Received, July* 10*th*, 1967; *Com.* 711.)

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