

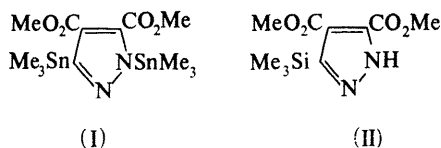
## Heterocyclic Syntheses with the Co-ordinated Ligand $\text{CN}_2^{2-}$ ; Reactions of Bistrimethylstannyldiazomethane and Trimethylsilyldiazomethane

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RECENTLY we reported the synthesis of the volatile organometallic diazomethanes  $\text{Me}_3\text{MCHN}_2$  ( $\text{M} = \text{Sn}$  or  $\text{Si}$ ), and showed that the tin compound, acting presumably as a 1,3-dipole, formed an adduct with phenyl isocyanate.<sup>1</sup> Similarly the silicon analogue reacts with acrylonitrile.<sup>2</sup>

We now present preliminary results (see Table) of a more extensive study of 1,3-dipolar reactions. Their significance is in that they provide a general synthesis for a variety of five-membered ring heterocycles, and also lead to a revision of the structure of the stannyldiazomethane.



The stannyldiazomethane, b.p.  $64\text{--}67^\circ/0.1\text{ mm.}$ ,  $\nu_{\text{max}}$   $2000\text{ cm.}^{-1}$  is  $(\text{Me}_3\text{Sn})_2\text{CN}_2$ , while the silicon compound, b.p.  $94\text{--}96^\circ/760\text{ mm.}$ ,  $\nu_{\text{max}}$   $2070\text{ cm.}^{-1}$ , is confirmed as  $\text{Me}_3\text{SiCHN}_2$ . The evidence, apart from analytical and spectral data, is as follows. (i) The products of reactions with 1,3-dipolarophiles AB usually (see Table) have molecular formulae (analysis and mass spectra)  $(\text{Me}_3\text{Sn})_2\text{CN}_2\cdot\text{AB}$ . (ii) The mass balance in these reactions and in another  $[2\text{Me}_3\text{SnNMe}_2 + \text{CH}_2\text{N}_2 \rightarrow (\text{Me}_3\text{Sn})_2\text{CN}_2 + 2\text{Me}_2\text{NH}]$  is consistent with the formula  $(\text{Me}_3\text{Sn})_2\text{CN}_2$ . (iii) This formula also agrees with the volume of gas ( $\text{N}_2 + \text{CH}_4 + \text{C}_2\text{H}_6 + \text{C}_3\text{H}_8$ ) and its composition (g.l.c.) from hydrolysis<sup>1</sup> of the stannyldiazomethane.

The new heterocyclic syntheses comprise the use of the following consecutive operations: conversion of  $\text{CH}_2\text{N}_2$  into  $(\text{Me}_3\text{Sn})_2\text{CN}_2$ , reaction of the latter with a 1,3-dipolarophile

AB (see Table), and protodestannylation [it is found that the adducts  $(\text{Me}_3\text{Sn})_2\text{CN}_2\cdot\text{AB}$  are readily protodestannylated to give the parent heterocycles  $\text{H}_2\text{CN}_2\cdot\text{AB}$  in  $5\text{M-HCl}$ ]. For example, structures (I) and (II) are suggested for the adducts of  $(\text{Me}_3\text{Sn})_2\text{CN}_2$  and  $\text{Me}_3\text{SiCHN}_2$  with  $\text{MeO}_2\text{C}\cdot\text{C}:\text{C}\cdot\text{CO}_2\text{Me}$ . As for the second step,  $(\text{Me}_3\text{Sn})_2\text{CN}_2$  is considerably more reactive than  $\text{CH}_2\text{N}_2$ ; and in none of the reactions so far examined with the tin compound is loss of nitrogen observed [cf. (Table),  $\text{CH}_2\text{N}_2$  and  $\text{Me}_3\text{SiCHN}_2$ ]. It is possible that for  $\text{AB} = \text{ArCN}$ , there is analogy with Hoberg's observation<sup>3</sup> of aluminium alkyl catalysis in the  $\text{ArCN-CH}_2\text{N}_2\text{-AlR}_3$  triazole synthesis; while it was proposed<sup>3</sup> that the function of the aluminium compound was to behave as a Lewis acid and thereby to activate the nitrile by co-ordination, it is possible that an organoaluminium diazomethane is initially formed which then reacts with the nitrile.

It is clear (see Table; the new protic and metallic adducts shown were analytically pure) that the reactivity of the  $\text{CN}_2^{2-}$  ligand with respect to its 1,3-dipolar addition reactions is significantly governed by the nature of the groups attached to carbon. With  $(\text{Me}_3\text{Sn})_2\text{CN}_2$ , the dipolar structure  $(\text{Me}_3\text{Sn})_2\text{C}^-\text{N}=\text{N}^+$  is probably particularly important as it may be stabilised by delocalisation of the negative charge on carbon.

The protodestannylation (cleavage of  $\text{Sn-C}$  and  $\text{Sn-N}$  bonds) of compounds such as (I) requires unexpectedly mild conditions, and is a much more ready process than the analogous protodesilylation of compounds such as (II). The ease of breaking  $\text{Sn-CN}_2$  bonds is further illustrated by conversion of  $(\text{Me}_3\text{Sn})_2\text{CN}_2$ , by treatment at room temperature with an acidic hydrocarbon  $\text{HY}$ , e.g.  $\text{HY} = \text{PhC}:\text{CH}$  or  $\text{C}_6\text{H}_6$ , into  $\text{Me}_3\text{SnY}$ .

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### M.p.'s of heterocycles with yields in parentheses

1,3-Dipolarophile	Diazomethane reagent		
	$\text{CH}_2\text{N}_2$	$\text{Me}_3\text{SiCHN}_2$	$(\text{Me}_3\text{Sn})_2\text{CN}_2$
<i>p</i> -TolN=C=NTol- <i>p</i>	161—162° (33%)	118—119° (19%)	132° (96%)
PhNCS	172.5 <sup>a</sup>	Loss of $\text{N}_2$	124—125 (82%)
$\text{CS}_2$	Loss of $\text{N}_2$ <sup>b</sup>	Loss of $\text{N}_2$	96 (80%)
PhNCO	Loss of $\text{N}_2$ <sup>c</sup>	Loss of $\text{N}_2$	d
PhCN	No reaction <sup>e</sup>	No reaction	d
$\text{MeO}_2\text{C}\cdot\text{C}:\text{C}\cdot\text{CO}_2\text{Me}$	141 <sup>f</sup>	78—80 (decomp.) (75%)	120—125 (decomp.) (91%)
$\text{CH}_2:\text{CHCN}$	100 (decomp.) <sup>g</sup>	54—56 (73%) <sup>h</sup>	120—125 (decomp.) (70%)
$\text{CH}_2:\text{CMe}\cdot\text{CN}$	(decomp.) <sup>l</sup>	9—10(64%)	60 (decomp.) (61%)

<sup>a</sup> H. v. Pechmann, *Ber.*, 1895, **28**, 860; <sup>b</sup> R. Rotter and E. Schaudy, *Monatsh.*, 1926, **47**, 493; <sup>c</sup> J. C. Sheehan and P. T. Izzo, *J. Amer. Chem. Soc.*, 1948, **70**, 1985; 1949, **71**, 4059; <sup>d</sup> Insoluble, polymeric (?) material obtained; <sup>e</sup> See ref. 3; <sup>f</sup> H. v. Pechmann, *Ber.*, 1899, **32**, 2299; <sup>g</sup> S. M. Gurvich and A. P. Terent'ev, *Sbornik Statei Obshchei Khim., Akad. Nauk. S.S.S.R.*, 1953, **1**, 409; <sup>h</sup> See ref. 2; <sup>i</sup> D. Gotkis and J. B. Cloke, *J. Amer. Chem. Soc.*, 1934, **56**, 2710.

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<sup>1</sup> M. F. Lappert and J. Lorberth, *Chem. Comm.*, 1967, 836.

<sup>2</sup> D. Seyferth, A. W. Dow, H. Menzel, and T. C. Flood, *J. Amer. Chem. Soc.*, 1968, **90**, 1080.

<sup>3</sup> H. Hoberg, *Annalen.*, 1967, **707**, 147.