Heterocyclic Syntheses with the Co-ordinated Ligand CN_2^{2-}; Reactions of Bistrimethylstannyldiazomethane and Trimethylsilyldiazomethane

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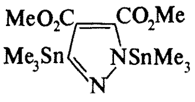
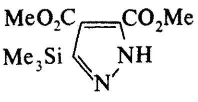
RECENTLY we reported the synthesis of the volatile organometallic diazomethanes Me_3MCHN_2 (M = Sn or Si), and showed that the tin compound, acting presumably as a 1,3-dipole, formed an adduct with phenyl isocyanate.[1] Similarly the silicon analogue reacts with acrylonitrile.[2]

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.



(I)



(II)

The stannyldiazomethane, b.p. 64—67°/0·1 mm., ν_{max} 2000 cm.$^{-1}$ is $(Me_3Sn)_2CN_2$, while the silicon compound, b.p. 94—96°/760 mm., ν_{max} 2070 cm.$^{-1}$, is confirmed as Me_3SiCHN_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) $(Me_3Sn)_2CN_2$,AB. (ii) The mass balance in these reactions and in another $[2Me_3SnNMe_2 + CH_2N_2 \rightarrow (Me_3Sn)_2CN_2 + 2Me_2NH]$ is consistent with the formula $(Me_3Sn)_2CN_2$ (iii) This formula also agrees with the volume of gas $(N_2 + CH_4 + C_2H_6 + C_3H_8)$ and its composition (g.l.c.) from hydrolysis[1] of the stannyldiazomethane.

The new heterocyclic syntheses comprise the use of the following consecutive operations: conversion of CH_2N_2 into $(Me_3Sn)_2CN_2$, reaction of the latter with a 1,3-dipolarophile AB (see Table), and protodestannylation [it is found that the adducts $(Me_3Sn)_2CN_2$,AB are readily protodestannylated to give the parent heterocycles H_2CN_2,AB in 5M-HCl]. For example, structures (I) and (II) are suggested for the adducts of $(Me_3Sn)_2CN_2$ and Me_3SiCHN_2 with $MeO_2C{\cdot}C\vdots C{\cdot}CO_2Me$. As for the second step, $(Me_3Sn)_2CN_2$ is considerably more reactive than CH_2N_2; and in none of the reactions so far examined with the tin compound is loss of nitrogen observed [*cf.* (Table), CH_2N_2 and Me_3SiCHN_2]. It is possible that for AB = ArCN, there is analogy with Hoberg's observation[3] of aluminium alkyl catalysis in the $ArCN–CH_2N_2–AlR_3$ triazole synthesis; while it was proposed[3] 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 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 $(Me_3Sn)_2CN_2$, the dipolar structure $(Me_3Sn)_2\overset{-}{C}–N{=}\overset{+}{N}$ is probably particularly important as it may be stabilised by delocalisation of the negative charge on carbon.

The protodestannylation (cleavage of Sn–C and 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 $Sn–CN_2$ bonds is further illustrated by conversion of $(Me_3Sn)_2CN_2$, by treatment at room temperature with an acidic hydrocarbon HY, *e.g.* HY = $PhC\vdots CH$ or C_5H_6, into Me_3SnY.

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

1,3-Dipolarophile	Diazomethane reagent		
	CH_2N_2	Me_3SiCHN_2	$(Me_3Sn)_2CN_2$
p-TolN=C=NTol-p	161—162° (33%)	118—119° (19%)	132° (96%)
PhNCS	172·5[a]	Loss of N_2	124—125 (82%)
CS_2	Loss of N_2[b]	Loss of N_2	96 (80%)
PhNCO	Loss of N_2[c]	Loss of N_2	d
PhCN	No reaction[e]	No reaction	d
$MeO_2C{\cdot}C\vdots C{\cdot}CO_2Me$	141[f]	78—80 (decomp.) (75%)	120—125 (decomp.) (91%)
$CH_2{:}CHCN$	100 (decomp.)[g]	54—56 (73%)[h]	120—125 (decomp.) (70%)
$CH_2{:}CMe{\cdot}CN$	(decomp.)[i]	9—10(64%)	60 (decomp.) (61%)

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

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[3] H. Hoberg, *Annalen.*, 1967, **707**, 147.