Now the total \([\text{Os(VIII)}]\) at any time may be given by Eq. (6)
\[
[\text{OsO}_\text{Total}] = [C_1] + [C_2] + [C_3] \tag{6}
\]
Also under the equilibrium conditions
\[
[C_1] = \frac{[C_2]}{K_1 [\text{OH}^-]} \tag{7}
\]
and
\[
[C_1] = \frac{[C_2]}{K_2 [\text{MA}]} \tag{8}
\]
By substituting the values of \([C_2]\) and \([C_1]\) in Eq. (6) and solving it in terms of \([C_2]\), the value of \([C_2]\) in terms of \([\text{OsO}_\text{Total}]\) has been obtained as,
\[
[C_2] = \frac{K_1 K_2 [\text{MA}] [\text{OH}^-] [\text{OsO}_\text{Total}]}{1 + K_1 [\text{OH}^-] (1 + K_2 [\text{MA}])} \tag{9}
\]
and, therefore, the rate of disappearance of oxidant may be represented by equation (9).
\[
\frac{d [\text{oxidant}]}{dt} = 2k_2 K_1 K_2 [\text{MA}] [\text{OH}^-] [\text{oxidant}] [\text{OsO}_\text{Total}] \frac{1}{1 + K_1 [\text{OH}^-] (1 + K_2 [\text{MA}])} \tag{10}
\]
At lower \([\text{alkali}]\) and \([\text{methylamine}]\) where the approximations \(1 \gg K_1 [\text{OH}^-]\) and \(1 \gg K_2 [\text{MA}]\) hold good the rate law takes the form
\[
\frac{d [\text{oxidant}]}{dt} = 2k_2 K_1 K_2 [\text{MA}] [\text{OH}^-] [\text{OsO}_\text{Total}] [\text{oxidant}] \tag{11}
\]
The rate law (11) predicts first order dependence of rate in each methylamine, alkali, catalyst and oxidant which has been observed experimentally at lower \([\text{alkali}]\) and \([\text{methylamine}]\).

It is probable that at higher \([\text{methylamine}]\) and \([\text{alkali}]\) the intermediate \([C_2]\) reacts with \(\text{OH}^-\) in place of oxidant (step 4) to give product and thus at higher \([\text{methylamine}]\) and \([\text{alkali}]\) the step 4 may be represented as,
\[
[C_2] + \text{OH}^- \rightarrow \text{Os(VI)} + \text{Products.}
\]
In this case, the rate law (12) for disappearance of oxidant has been obtained.
\[
\frac{d [\text{oxidant}]}{dt} = \frac{k_2 K_1 K_2 [\text{MA}] [\text{OH}^-]^2 [\text{OsO}_\text{Total}]}{1 + K_1 [\text{OH}^-] (1 + K_2 [\text{MA}])} \tag{12}
\]
The rate law (12) suggests that at higher \([\text{alkali}]\) the order in oxidant would be zero. This is found to be experimentally true. The dependence of the rate on methylamine may be represented by Eq. (13)
\[
\text{Rate} \propto \frac{\text{constant} \times [\text{MA}]}{[1 + K_2 [\text{MA}]]} \tag{13}
\]
However, in such a case a plot of \(1/\text{rate constant}\) versus \(1/[\text{methylamine}]\) would be linear with a positive intercept. This is in accord with the experimental observation.

Further, at higher \([\text{alkali}]\) the order in alkali would increase from unity and would lie between one and two. The values of \(K_2/[\text{OH}^-]\) obtained at different \([\text{alkali}]\), where the order in oxidant is unity, are as 0.495, 0.536, 0.533, 0.575 and 0.44\times 10^{-2} \text{ mol}^{-1} \text{ litre sec}^{-1} \) at 0.04, 0.06, 0.08, 0.10 and 0.15 M NaOH respectively. The values of \(K_2/[\text{OH}^-]\) obtained, where the order in oxidant is zero (Fig. 2), are 1.66, 2.40 and 2.50 \times 10^{-4} \text{ sec}^{-1} \) at 0.15, 0.20 and 0.30 M NaOH respectively. These values clearly indicate that the order in alkali increases from unity at higher \([\text{alkali}]\).

Thus the experimental results are in complete agreement with the above rate law equation (12) at higher concentrations of alkali and methylamine.

As the rate-determining step (3) involve a neutral molecule (methylamine), a negligible salt effect is expected which has also been obtained experimentally.

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Insertion Reactions of Some Unsaturated Substrates Across Metal-Nitrogen Bonds in Dibutylmetal(III) Azides

T. N. SRIVASTAVA, R. C. SRIVASTAVA & (Mrs) KIRAN SINGHAL
Chemistry Department, Lucknow University, Lucknow 226 007

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Insertion reactions of unsaturated substrates, viz. phenyl isothiocyanate, phenyl isocyanate, benzonitrile and carbon disulphide across metal-nitrogen bond of dibutylmetal(III) azides, Bu2MNa3 (M = gallium, indium and thallium) have been studied. The products have been characterized by IR, UV and PMR and elemental data. The contrasting behaviour of carbon disulphide towards dibutylmetal(III) azides and possible mechanisms for such reactions are also discussed.

INSERTION reactions across boron-nitrogen or aluminium-nitrogen bond in boron or aluminium amides are reported in the literature1-4. However similar reactions involving M(III)-N bond (M = Ga, In and Tl) do not seem to have received much attention. In continuation of our studies4 on organome-
tallic pseudohalides and their acceptor property we report in this note the reaction of dibutylmetal (III) azides with unsaturated substrates, viz. carbon disulphide, phenyl isothiocyanate, phenyl isocyanate and benzonitrile.

Dibutylmetal(III) azides (M = Ga, In and Tl) were prepared by reported procedures. Phenyl isothiocyanate, phenyl isocyanate and benzonitrile (BDH) were distilled before use. Carbon disulphide was dried over molecular sieves.

Two representative reactions of dibutylmetal(III) azides with the unsaturated substrates are described below. Details are given in Table 1.

(i) Dibutylindium azide (2.7 g, 0.01 mol) and phenyl isothiocyanate (1.3 g, 0.01 mol) were heated together at 120° for 8 hr. The resulting brown residue was extracted with boiling hexane. The extract on cooling gave white crystals of 1-phenyl-4-(dibutylindium)-tetrazole-4-thione. m.p. 182°.

(ii) Dibutylgallium azide (2.27 g, 0.01 mol) was stirred in refluxing carbon disulphide (5 ml) for 12 hr and filtered to remove elemental sulphur (m.p. 120°, lit m.p. 120°). The filtrate on concentration yielded dibutylgallium isothiocyanate, m.p. 105°.

Similar experiments with diphenyl-gallium, -indium or -thallium azide resulted in their quantitative recovery even after 15 hr refluxing.

Dibutylgallium, -indium and -thallium azides react with phenyl isothiocyanate, phenyl isocyanate and benzonitrile under different conditions to yield 1-phenyl-4-(dibutylmetal)-tetrazole-5-thione (Ia-c), 1-phenyl-4-(dibutylmetal)-5-tetrazolinone (Id-f) or 1-phenyl-4-(dibutylmetal)-5-tetrazole (Iia-c) derivatives.

The reaction with phenyl isocyanate is more facile than with phenyl isothiocyanate. The compounds (I) and (II) obtained in 40-50% yields are white to brown solids except Iic which is obtained as a sticky mass. They are unaffected by air and moisture.

Evidence in favour of cyclic structure (I) has mainly been derived from the spectroscopic data.

The formation of dibutylmetal(III) azide adducts with PhNCX or PhCN, either coordination through N, O or C is ruled out since the IR spectra (Perkin-Elmer model 177, vmax in cm−1) do not show characteristic absorptions for the azido group around 2040. The products exhibit a band in the region 1305-1265 of variable intensity assignable to the cyclic-N = N = N linkages. The symmetric azide stretching usually of weak intensity also appears in the same region but Lieber et al. from a study of several tetrazole derivatives, have assigned the absorption in the range 1300-1270 to cyclic -N=N-N stretching. The formation of the cyclic product is further supported by the absence of N=C=S, (N=C=O) or (C=N) absorption around 2080, 1175 for 2100 respectively, and the appearance of a new band due to v C=S at 1395-1310 (ref. 6) and due v (C=O) around 1700 (ref. 10). A new band of weak intensity between 1100 and 1000 may be assigned to skeletal mode of vibration of the tetrazole

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**Table 1 — Analytical Data for the Reaction Products of Unsatuated Substrates With Dibutylmetal(III) Azides**

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Reaction period (hr) and temp. (°C)</th>
<th>Product‡</th>
<th>m.p. °C</th>
<th>Found (%) (Calc.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga PhNCS</td>
<td>10(140)</td>
<td>Ia</td>
<td>114</td>
<td>49.86 (6.38) (15.50) (19.70)</td>
</tr>
<tr>
<td>In PhNCS</td>
<td>8(120)</td>
<td>Ib</td>
<td>182</td>
<td>44.62 (5.63) (13.91) (28.18)</td>
</tr>
<tr>
<td>Tl PhNCS</td>
<td>6(100)</td>
<td>Ic</td>
<td>127</td>
<td>36.72 (4.68) (11.36) (41.25)</td>
</tr>
<tr>
<td>Ga PhNCO</td>
<td>2(140)</td>
<td>Id</td>
<td>240d</td>
<td>52.08 (6.62) (16.13) (20.57)</td>
</tr>
<tr>
<td>In PhNCO</td>
<td>2(140)</td>
<td>Je</td>
<td>128</td>
<td>46.22 (5.93) (14.42) (29.36)</td>
</tr>
<tr>
<td>Tl PhNCO</td>
<td>1(80)</td>
<td>If</td>
<td>114</td>
<td>37.52 (4.85) (11.50) (42.61)</td>
</tr>
<tr>
<td>Ga PhCN</td>
<td>3(100)</td>
<td>Iia</td>
<td>119</td>
<td>54.54 (6.93) (17.03) (21.58)</td>
</tr>
<tr>
<td>In PhCN</td>
<td>3(140)</td>
<td>IIb</td>
<td>121</td>
<td>48.29 (6.16) (15.11) (30.52)</td>
</tr>
<tr>
<td>Ti PhCN</td>
<td>6(140)</td>
<td>IIC</td>
<td>sticky mass</td>
<td>—</td>
</tr>
<tr>
<td>Ga S=C=S</td>
<td>12(46)</td>
<td>IIIa</td>
<td>105</td>
<td>44.41 (7.46) (5.75) (29.29)</td>
</tr>
<tr>
<td>In S=C=S</td>
<td>10(46)</td>
<td>IIIb</td>
<td>240d</td>
<td>37.70 (6.28) (4.86) (39.76)</td>
</tr>
<tr>
<td>Tl S=C=S</td>
<td>14(46)</td>
<td>IIIc</td>
<td>Explodes</td>
<td>—</td>
</tr>
</tbody>
</table>

‡Yield 40-50%
ring as reported earlier. Three following resonating structures for the compounds may be suggested.

Reactions of CS₂ with dibutylmetal azides instead of cyclic products yield dibutylmetal (III) isothiocyanates, giving elemental sulphur and gaseous nitrogen. Diphenylgallium, -indium and -thallium azides however fail to react with CS₂. The formation of dibutylmetal isothiocyanate is indicated by the disappearance of a sharp band around 2040, characteristic of azido group and the appearance of relatively broad band around 2030.

The UV absorption spectra (Perkin-Elmer model 202; 1 cm quartz cell in methanol) of Iff and IIb showed two multiplets each centred at 268 nm similar to that exhibited by 1-phenyl tetrazolines, giving elemental sulphur and gaseous nitrogen.

Withdrawing groups and metal azide possesses electron withdrawing groups. The failure of the reaction of CS₂ with phenylazides (M=Ga, In and Tl) may partly be, due to the electron withdrawing effect of phenyl rings, since alkyl-metal compounds react readily.

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Some New p-Fluoro- & p-Chloro-benzoilacetonate Derivatives of Tri- & Di-organotin(IV) & Tin(IV)

R. R. JAIN, J. C. MAIRE†, Y. MAIRE-LIMOUZIN†, A. BALDY† & B. P. BACHLAS*  
Department of Chemistry, University of Rajasthan, Jaipur 302004

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Five- and six-coordinated, covalent and monomeric complexes of tri- and di-organotin(IV) of the type $R_2Sn(p-XC_6H_4COCHCOCH_2)$ and $R_2Sn(p-XC_6H_4COCHCOCH_2)$, where $R = CH_3$, $C_2H_5$, $n-C_3H_7$, $n-C_3H_7$, $n-C_3H_7$, $n-C_3H_7$, and $X = F$, Cl, have been synthesised and characterised. Ion-pair and covalent type complexes of Sm(IV), [(Cl)Sn(p-XC_6H_4COCHCOCH_2)]$^{+}$ and Y$_2$Sn (p-XC_6H_4COCHCOCH_2)$_2$, $X = Cl, Br, Y = Cl, Br, I], have also been synthesised.

INtErEst in the coordination chemistry of organotin(IV) and tin (IV) has mainly centred around syntheses, isolation, characterisation and stereochemistry of (a) Lewis acid-base adducts and (b) coordinated derivatives involving bidentate ligands containing oxygen, nitrogen and sulphur donor atoms.

As a part of our project on the reactions of group (IV) non-transition metal and organometallic chlorides with p-halo (F,Cl, Br) benzoylacetonates and 2-thienoyl trifluoroacetonates this paper reports the reactions of p-fluoro- and p-chloro-benzoilacetonates.

†Laboratoire des Organometalliques-Faculte des Sciences et Techniques de Saint-jerome, Universite de Droit, d'Economie et des Sciences d'Aix-Marseille 13397 MARSEILLE Cedex 4 (France).