PHOTOLYSIS OF AZIDOTRIPHENYL DERIVATIVES OF GERMANIUM, TIN AND LEAD

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The controlled photochemical or thermal degradation of organic azides invariably<sup>1</sup> provides a route to nitrenes:  $RN_3 \longrightarrow R\overline{N}$  or  $R\overline{N} + N_2$ 

Azidotriphenylmethane (I) under these conditions is converted to benzophenonephenylimine<sup>2</sup>:

$$\frac{Ph_{3}MN_{3}}{(\text{stepwise via nitrene})} \xrightarrow{Ph_{2}C = NPh + N_{2}}$$

$$Ph_{3}MN_{3}$$
, M = C(I), Si(II), Ge(III), Sn(IV), Pb(V)

Extensive work has been reported<sup>3,4</sup> on organometallic pseudohalides including azido derivatives of Si,Ge,Sn, and Pb; thermolysis of II - V proceeds in the following fashion<sup>5</sup>: II  $\longrightarrow$  N<sub>2</sub> + Ph<sub>3</sub>SiNI  $\longrightarrow$  Ph<sub>2</sub>Si - NPh

III ---> "polymeric material containing phenyl groups bound to nitrogen".

$$IV \longrightarrow Ph_4Sn + N_2$$
$$V \longrightarrow Ph_4Pb + N_2$$

The photolysis of II-V and related<sup>5</sup> compounds has received little attention; Reichle<sup>6</sup>, and Thayer and West<sup>7</sup> reported that photolysis of II (2537Å) caused some decomposition but did not isolate any pure products. In view of the possibility<sup>8</sup> of unusual metal-azide bonding in these compounds we considered it of interest<sup>9</sup> to examine their photolysis with a view to assessing the relative reactivity of intermediates of the type  $Ph_xM\bar{N}$  (M=Ge,Sn,Pb)

Photolyses (SCHEME) were carried out on 2-5% solutions in dichloromethane or tetrahydrofuran (THE) using a lamp emitting <u>ca</u>. 50% irradiation at 2537Å.

SCHEME



$$\frac{Ph_4Pb(19\%)}{+uncharacterised polymer} \underbrace{THF}_{(b)} V \underbrace{CH_2Cl_2}_{Ph_3PbCl(75\%)}$$

\* Yield based on consumed azide.

The predominant process in methylene chloride solvent appears to involve an initial homolysis of the type

 $Ph_{3}MN_{3} \longrightarrow Ph_{3}M^{\circ} + N_{3}^{\circ}$  followed by chlorine abstraction from the relatively labile C-Cl bond:

By analogy with the thermal decomposition, reactions (a) and (b) produce tetraphenyl derivatives of tin and lead, albeit in low yield. The isolation of deep red oils from all the reactions attempted  $\begin{bmatrix} \lambda & \text{EtOH} \\ \text{max}(\text{sh}) & \underline{\text{ca.}}325-340\text{mu}, & \underline{\text{cf.}} & \lambda & \text{max} \text{ for } -N=N-\underline{\text{ca.}} & 338\text{mu} \end{bmatrix}$  suggests that minor decomposition mode of the type  $Ph_3 & \text{MN}_3 \longrightarrow N_2 + Ph_3 & \text{MN} = NMPh_3$ operates; as yet we have been unable to purify the coloured products but we are investigating reactions of this type on a wider basis as a route to organometallic azo compounds.

## EXPERIMENTAL

 $III^8$ ,  $IV^8$ , and  $V^{10}$  were prepared by literature methods and photolysed in dry solvents using a silica flask and a lamp emitting <u>ca.</u> 50% irradiation at 2537Å; decomposition was followed by observing decrease in intensity of the azide asymmetric stretching band<sup>8</sup> at ca. 2100 cm<sup>-1</sup>.

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