Preliminary communication

Reactions of bis(trifluoromethyl)nitroxide with tris(fluoromethyl)-phosphine and -arsine

H.G. ANG and K.F. HO Chemistry Department, University of Singapore, Singapore, 10 (Received August 4th, 1969)

Bis(trifluoromethyl)nitroxide (I), first synthesised by Blackley and Reinhard¹, has been shown to be both an excellent hydrogen abstractor and a free radical scavenger^{2,5}. Its readiness to react with many metals has also led to the synthesis of several metal derivatives which have been used as reactive intermediates³. Reactions of the nitroxide (I) are now extended to a number of Group V compounds containing trifluoromethyl groups.

The nitroxide (I) reacts with tris(trifluoromethyl)phosphine (II) to give an addition compound, $(CF_3)_3P[ON(CF_3)_2]_2$. No radical exchange reaction is observed here, in contrast to reactions which occur between the phosphine (II) and either methyl iodide or *N*-halogenobis(trifluoromethyl)amine⁴. Bis(trifluoromethyl)chlorophosphine also undergoes an addition reaction with the nitroxide (I) to afford $(CF_3)_2 PCI[ON(CF_3)_2]_2$. The formation of phosphoranes (V) rather than trivalent phosphorus derivatives, seems to be a general with phosphorus compounds containing electronegative trifluoromethyl substituents⁵. On the other hand, tris(trifluoromethyl)arsine displays stepwise substitution reactions which can be represented by the following equations:

$$2(CF_{3})_{2} \text{ NO} + (CF_{3})_{3} \text{ As} \xrightarrow{\text{r.t.}} (CF_{3})_{2} \text{ AsON}(CF_{3})_{2} + (CF_{3})_{2} \text{ NOCF}_{3}$$

r.t. 2(CF_{3})_{2} NO
(4/1)r.t. CF_{3} \text{ As}[ON(CF_{3})_{2}]_{2} + (CF_{3})_{2} \text{ NOCF}_{3}
70° 2(CF_{3})_{2} NO
(6/1)70° [(CF_{3})_{2} NO]_{3} \text{ As} + (CF_{3})_{2} \text{ NOCF}_{3}

(r.t., room temperature)

Reactions of the nitroxide (I) with tris(trifluoromethyl)-phosphine and -arsine seem to suggest that its properties are akin to those of chlorine⁶.

 $[(CF_3)_2 NO]_3 As and (CF_3)_2 NOAs(CF_3)_2$ have also been prepared by the

J. Organometal. Chem., 19 (1969) P19-P20

reactions of the nitroxide (I) with arsenic metal and bis(trifluoromethyl)arsine respectively⁵. $[(CF_3)_2NO]_3As$ reacts with one mole of hydrogen chloride to give $[(CF_3)_2NO]_2AsCl$ and bis(trifluoromethyl)hydroxylamine. Except for $[(CF_3)_2NO]_3As$, the other bis(trifluoromethyl)nitroxide derivatives of phosphorus and arsenic are liquids at room temperature. All the compounds have been characterised by elemental analysis, and confirmed by their IR spectra and, in some cases, by their molecular weights using Reynault's method.

Further radical exchange reactions with other Group V compounds are in progress.

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