Journal of Fluorine Chemistry, 3 (1973/74) 235–236

Preliminary Note

Addition reactions of substituted arsines and stibine with bis(trifluoromethyl)nitroxyl

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(Received January 12, 1973)

It has been shown that tris(trifluoromethyl)arsine undergoes stepwise exchange reactions with bis(trifluoromethyl)nitroxyl to yield a series of derivatives of the type $[(CF_3)_2NO]_nAs(CF_3)_{3-n}$ where $n = 1, 2, 3$, together with tris(trifluoromethyl)hydroxylamine[1]. We report that the reaction between bis(trifluoromethyl)nitroxyl and methylbis(trifluoromethyl)arsine in the ratio 2:1 proceeds to give predominantly two pentavalent arsenic derivatives which bear the formula $[(CF_3)_2NO]_2AsCH_3(CF_3)_2$. Radical-exchange reaction also occurs, but only to a limited extent. Both the reactions can be represented by the following equations:

$$(CF_3)_2AsCH_3 + 2(CF_3)_2NO \rightarrow [(CF_3)_2NO]_2AsCH_3(CF_3)_2 \quad (1)$$

$$(CF_3)_2AsCH_3 + 2(CF_3)_2NO \rightarrow (CF_3)_2NOAsCH_3CF_3 + (CF_3)_2NOCF_3 \quad (2)$$

The pentacovalent derivatives of arsenic are trapped at $-10°$ (but passed at 0°) under vacuum fractionation. This fraction was found to consist of two isomers which are effectively separated by fractional crystallisation. One isomer has a melting point of 22° and the other a melting point of 33° under vacuum.

In the reaction shown in equation (2), one trifluoromethyl group instead of the methyl group is involved in the exchange. The overriding factor here is presumably a statistical one.

On extending similar reactions to dimethyltrifluoromethylarsine, only one isomeric addition product, $[(CF_3)_2NO]_2As(CH_3)_2CF_3$, is formed. On the other hand, the reaction with trimethylarsine gives two isomeric addition products bearing the formula $[(CF_3)_2NO]_2As(CH_3)_3$. No exchange is observed in the above reactions.

It has been found that the reaction with trimethylstibine also gives an addition compound, namely $[(CF_3)_2NO]_2Sb(CH_3)_3$. This observation is quite unlike the exchange reaction reported with tris(trifluoromethyl)stibine[2].

All the new compounds have been characterised by elemental analysis, and subsequently confirmed by infrared spectra and chemical reactions. Thus, it is found that with all pentacovalent bis(trifluoromethyl)nitroxy derivatives of arsenic and antimony, the reactions with hydrogen chloride cleave the metal–oxygen bonds to give a quantitative conversion to bis(trifluoromethyl)hydroxylamine and the corresponding dichloride, as illustrated below:

$$[(CF_3)_2NO]_2As(CH_3)_3 + 2HCl \rightarrow (CF_3)_3AsCl_2 + 2(CF_3)_2NOH$$

Moreover, hydrolysis with 20% sodium hydroxide eliminates fluoroform in excellent yields from arsenic derivatives containing trifluoromethyl group(s) bonded to the metal.

The above findings involving the reactions between bis(trifluoromethyl)-nitroxyl and various substituted arsines and stibine permit the following conclusions to be drawn:

(a) Exchange reactions are favoured by compounds such as $(CF_3)_3M$ (M = As and Sb), where all the substituents are highly electronegative.

(b) The introduction of electropositive methyl groups to arsenic or antimony seems to promote addition reactions.

REFERENCES

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