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PRELIMINARY NOTE

NOVEL REACTIONS INVOLVING O-NITROSOBIS(TRIFLUOROMETHYL)HYDROXYLAMINE
WITH $M(\text{CF}_3)_3$ (M = P, As and Sb) AND SOME OLEFINS

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SUMMARY

O-Nitrosobis(trifluoromethyl)hydroxylamine gives novel reactions with tris(trifluoromethyl)phosphine, -arsine and -stibine to afford mainly the corresponding bis(trifluoromethyl)nitroxy derivatives. Tris(trifluoromethyl)phosphine affords $(\text{CF}_3)_2\text{NOP}(\text{O})(\text{CF}_3)_2$ and $(\text{CF}_3)_2\text{NNO}$. Tris(trifluoromethyl)arsine also gives $(\text{CF}_3)_2\text{NNO}$ in high yield, together with smaller amounts of $(\text{CF}_3)_2\text{NOAs}(\text{CF}_3)_2$, $\text{CF}_3\text{N} = \text{CF}_2$, COF_2 and a polymeric white solid. With tris(trifluoromethyl)stibine, no oxidation nor addition reactions occurred. Instead, $[(\text{CF}_3)_2\text{NO}]_3\text{Sb}$ and $[(\text{CF}_3)\text{NO}]_2\text{SbCF}_3$ were obtained in high yields. The stoichiometry of the reactions suggests that the additional amounts of bis(trifluoromethyl)nitroxy groups bonded to antimony are derived from the trifluoromethyl groups bonded to antimony. However, O-nitrosobis(trifluoromethyl)hydroxylamine gives addition products at room temperature with 1,1-difluoro-2,2-dichloroethylene and 1,1-difluoro-2-fluoro-2-bromoethylene. Mechanisms to rationalise the above reactions involving Group V compounds are proposed.

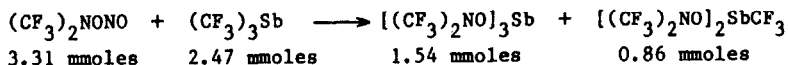
INTRODUCTION

To date only a few reactions of O-nitrosobis(trifluoromethyl)-hydroxylamine have been reported. These are the pyrolysis reactions [1, 2] as well as reactions with phosphorus pentachloride and S_2F_{10} [3]. We have found that the reactions of O-nitrosobis(trifluoromethyl)hydroxylamine with some olefins and $M(CF_3)_3$ ($M = P, As$ and Sb) are novel, and they proceed readily involving the cleavage of $(CF_3)_2NO-NO$ bond.

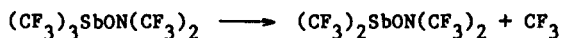
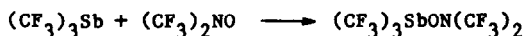
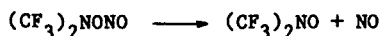
RESULTS

O-Nitrosobis(trifluoromethyl)hydroxylamine reacts with tris(trifluoromethyl)phosphine at a temperature range of 65 to 85°C, to give tris(trifluoromethyl)nitroxybis(trifluoromethyl)phosphine oxide, $(CF_3)_2NOP(O)(CF_3)_2$, and $(CF_3)_2NNO$. The reactions with tris(trifluoromethyl)arsine at 80°C afforded $(CF_3)_2NOAs(CF_3)_2$ and $(CF_3)_2NNO$, the latter in 97% yield. The other products were a trifluoromethyl-substituted polymeric solid together with smaller amounts of perfluoro-2-azapropene and carbonyl fluoride.

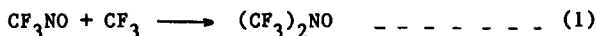
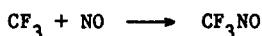
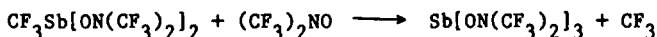
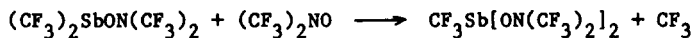
In the reactions with tris(trifluoromethyl)stibine at room temperature, two substituted stibines, namely $[(CF_3)_2NO]_2SbCF_3$ and $[(CF_3)_2NO]_3Sb$, were afforded in high yields. The stoichiometry of the reactions shows that the bis(trifluoromethyl)nitroxy groups attached to antimony are derived not only from O-nitrosobis(trifluoromethyl)hydroxylamine, but also from tris(trifluoromethyl)antimony, as indicated below:



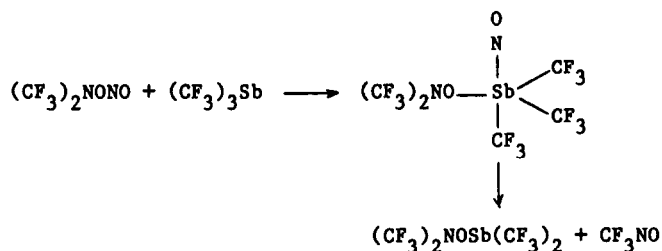
The formation of bis(trifluoromethyl)nitroxy groups from tris(trifluoromethyl)antimony probably occurs via the attack of trifluoromethyl radicals on the nitric oxide, according to the following reaction pathways:



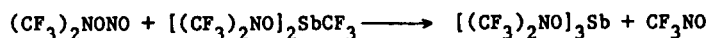
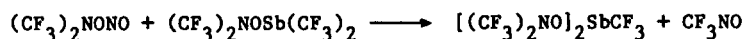
Similarly,



A concomitant mechanism which appears possible is that which leads to the formation of the pentavalent antimony intermediate followed by the elimination of trifluoronitrosomethane, as shown below:



Similarly,



The conversion of trifluoronitrosomethane to bis(trifluoromethyl)nitroxyl proceeds according to equation (1).

The ease of cleavage of the $(\text{CF}_3)_2\text{NO-NO}$ bond is again demonstrated when it gives a 1:1 deep blue liquid of the nitroso compounds, $(\text{CF}_3)_2\text{NO}-\overset{|}{\underset{|}{\text{C}}}-\overset{|}{\underset{|}{\text{C}}}-\text{NO}$, with bromotrifluoroethylene and 1,1 dichloro-2,2-difluoroethylene at room temperature.

REFERENCES

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- 2 Dinwoodie A.H. and Haszeldine R.N., J. Chem. Soc. A., 431 (1969).
- 3 Vorob'ev M.D., Filatov A.S. and Englin M.A., Zh. Obshch. Khim., 44 (12), 2724-7 (1974).