

A NEW SYNTHESIS OF DIFLUORAMINO TRIFLUOROMETHANE

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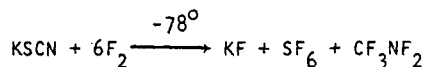
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SUMMARY

Fluorination of azidotrifluoromethane furnishes difluoramino trifluoromethane in a direct, reproducible, and high yield reaction. A maximum rate of conversion with minimum degradation was obtained at 70-80°. Enhancement of the rate of reaction was realized with added KF as a catalyst.

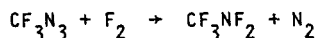
INTRODUCTION

Numerous methods have been reported[1,2]for the synthesis of difluoroamino trifluoromethane, CF_3NF_2 , including fluorination of amines, nitriles, metal cyanides, and metal thiocyanides. Fluorinating agents employed are NF_3 , N_2F_4 , transition metal fluorides, and fluorine. Nearly all these processes suffer from low yields of the desired CF_3NF_2 , poor reproducibility, and/or the presence of difficultly separable by-products. For example, many of the methods produce coproduct C_2F_6 whose b.p. is the same as that of CF_3NF_2 and thus it is very tedious to effect their separation. Ruff has reported [3] an excellent yield of CF_3NF_2 by the reaction shown.



However, half of the fluorine consumed goes to by-products and the small difference in the b.p.'s of SF_6 and CF_3NF_2 , 14°, requires chromatographic purification techniques.

It has now been discovered that a direct, reproducible, high yield synthesis of CF_3NF_2 is possible according to:



Minimal side reactions were encountered.

EXPERIMENTAL

Volatile materials were manipulated in a stainless-steel vacuum line equipped with Teflon FEP U traps and 316 stainless-steel bellows seal valves and a Heise Bourdon-Tube type gauge. Gas chromatographic data were obtained using a Varian GC under isothermal conditions with a stainless-steel column (1/8" X 10') packed with Poropak PS. Fluorine (Air Products) was scrubbed with NaF immediately before it was used. Trifluoromethyl azide was prepared by a previously described procedure [4,5].

Synthesis of CF_3NF_2 . A 30 ml stainless-steel Hoke cylinder was loaded with CF_3N_3 (1.68 mmol) and F_2 (6.70 mmol) at $-196^\circ C$. The cooling bath was removed and as soon as the cylinder was free of frost, it was placed in an oven preheated to $70^\circ C$. After 24 hours the reactor was cooled to -196° and all volatile material, consisting mainly of the excess F_2 and by-product N_2 , was pumped away. The condensable material (1.69 mmol) was shown by infrared spectroscopy and GC analysis at $65^\circ C$ to be 51% unreacted CF_3N_3 and 49% CF_3NF_2 with a trace of CF_4 . When fluorinated for an additional 24 hour period at $70^\circ C$, the yield of CF_3NF_2 was 84% and about 15% CF_3N_3 was still recovered. Further fluorination consumed the azide and produced CF_3NF_2 (92%), CF_4 (6%) and C_2F_6 (1-2%). A similar $70^\circ C$ fluorination reaction in which the reactor contained 18 mmol of anhydrous KF powder, gave a 68% yield of CF_3NF_2 after 1 day. After 2 days this yield had increased to 73% and was accompanied by a 6.4% yield of the degradation product CF_4 .

RESULTS AND DISCUSSION

Azidotrifluoromethane and difluoroamino trifluoromethane are potentially hazardous and should be handled with caution. The existence of CF_3N_3 has been known for some time [4], but its chemistry remained unexplored. In covalent azides, X-N-N-N, the N-N bond adjacent to the X group is longer and weaker than the other N-N bond [6]. In a fluorination reaction this is a likely fragmentation point and if controllable could be expected to lead to X-N-F derivatives. For CF_3N_3 this was expected to produce CF_3NF_2 . It was found that little or no reaction occurred with F_2 at $\leq 20^\circ$. Increasing the temperature, however, gave reproducible amounts of CF_3NF_2 . Percent conversions after 24 hours at various temperatures are shown in Figure 1.

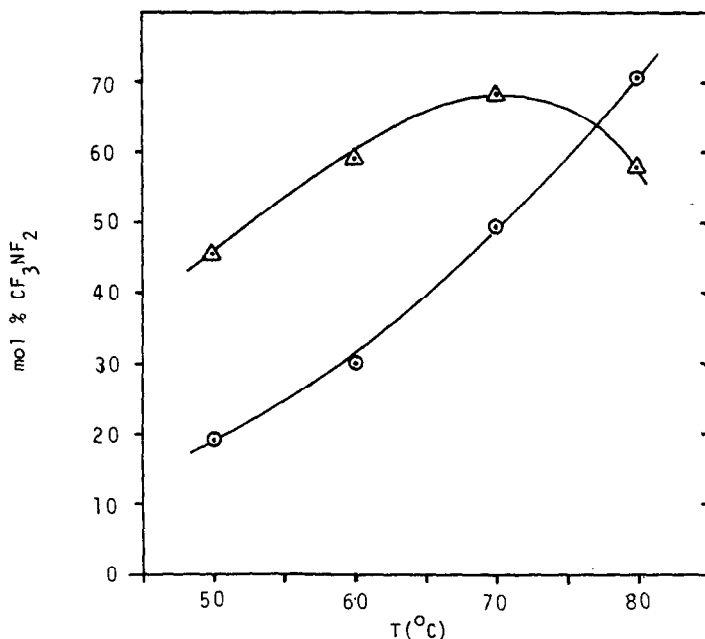
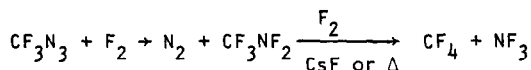


Fig. 1. Yield % CF_3NF_2 after 24 hours without (●) and with added KF (▲) as a catalyst.

Enhancement of the rate of reaction was realized with added KF, while CsF at 20°C or higher temperature lead to further fluorination as shown in the equation.



The maximum yield of CF_3NF_2 observed in both catalyzed and uncatalyzed reactions for 1 day was about 70%. After slightly longer reaction times yields are in the 90-95% range. In addition to the by-products CF_4 and NF_3 which are easily separated, there was also some C_2F_6 formed (~1%) when all the CF_3N_3 had reacted. Although not a very fast reaction, this synthesis has the advantages of high-yield, easy product purification, and reproducibility.

ACKNOWLEDGEMENT

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REFERENCES

- 1 J. K. Ruff, Chem. Rev., 67, 665 (1967).
- 2 J. P. Freeman, Adv. Fluorine Chem., 6, 287 (1970).
- 3 J. K. Ruff, J. Org. Chem., 32, 1675 (1967).
- 4 S. P. Makarov, A. Ya Yakubovich, A. S. Filatov, M. A. Englin, and T. Ya. NikiForova, Zh. Obshch. Khim., 38, 709 (1968).
- 5 K. O. Christe and C. J. Schack, Inorg. Chem., in press.
- 6 K. Jones in 'Comprehensive Inorganic Chemistry,' Vol. 2, J. C. Bailar et al Eds., Pergamon Press (1973) p. 281.