SHORT COMMUNICATION

A Simple High Yield Synthesis of trans-Difluorodiazene (trans-N_2F_2)

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Trans-N_2F_2 is a highly reactive compound and of interest as a high energy oxidizer, as a potential scavenger for radiokrypton [1], or as an initiating agent for polymerizations [2]. Its application as a fluorinating agent in organic chemistry has been described recently [3].

Many different synthetic methods for preparing trans-N_2F_2 are known. They are listed and compared in [4], where their relative disadvantages are discussed. All suffer from the drawback of not producing a pure isomer in high yield in one simple step, or only yield mixtures of cis- and trans-N_2F_2 [4].

During an extensive study [5] of the chemistry of AsF_5-graphite intercalation compounds [6] we found that fluorinated and unfluorinated first stage AsF_5 - intercalates: $C_{10}AsF_{5+x}$ (x = 0-0.5) converted N_2F_4 quantitatively into a mixture of 90% trans-N_2F_2, 5% NF_3 and 5% N_2. The reaction can be expressed by equation (1).

Blue   Black

$$C_{10}AsF_{5+x} + N_2F_4 = C_{10}AsF_{7+x} + \text{trans-}N_2F_2 \quad (x = 0\text{-}0.5) \quad (1)$$
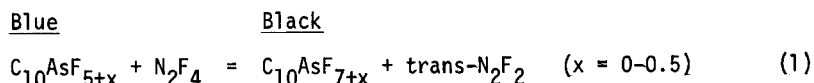
The results are listed in Table 1.

It is obvious that the reaction is carried out best with finely divided powdered intercalates. No difference in the reactivity between fluorinated and unfluorinated $C_{10}AsF_5$ has been observed.

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TABLE 1

The reaction of N_2F_4 with $C_{10}AsF_{6+x}$ (x = 0-0.5)

Starting Materials				Products		
Intercalate (Powder)	AsF_5 (mmol)	N_2F_4 (mmol)	time (days)	trans-N_2F_2(NF_3) (mmol)	average molecular weight (g)	non condensable gases (mmol)
$C_{10.3}AsF_5$	1.56	1.03	2	0.99	68	~ 0.04
$C_{10}AsF_5$	1.66	1.66	2	1.6	68	~ 0.1
$C_{9.36}AsF_{5.5}$	3.45	3.4	2	2.9	68	~ 0.3
$C_{10.6}AsF_{5.6}$	1	1	5	0.96	65	~ 0.05
$C_{10.6}AsF_{5.6}$	2	2	4.5	1.9	65	~ 0.1
Grafoil						
$C_{9.38}AsF_5$	3	3	1	No reaction after 1 day		
$C_{9.1}AsF_{5.5}$	3	3	13	1.7	72	

The identification of the gases was carried out by IR-spectroscopy [7][8], mass spectrometry [9][10] and molecular weight measurements. The composition of the gas phase was established by selective reduction with aqueous KI, leaving behind 5% NF_3 and by IR intensity measurements of the ν_3 band of NF_3 (907 cm^{-1}) [8] in comparison with calibrated NF_3 - spectra. The gas phase contains no impurities other than NF_3 ($\leq$ 5%).

The reaction ends after N_2F_4 is converted by an equivalent of intercalated AsF_5. This is best explained in terms of intermediate formation of the adduct $N_2F_3^+AsF_6^-$ [11] inside the graphite, followed by fluoride abstraction by the graphite. The reaction does *not* take place with the second or third stage compounds $C_{16}AsF_5$, $C_{24}AsF_5$.

Graphite powder (SP-1, Ceylon graphite min. purity 99.9%), obtained from Union Carbide Co., was used without further purification. AsF_5, obtained from Ozark-Mahoning, was purified by low temperature distillation. The experiments were conducted in a high vacuum metal line constructed from Monel and Nickel. Reactions were carried out in 3/4" pre-weighed Kel-F tubes sealed with 1/4" flare Kel-F valves. The amounts of N_2F_4 and products were determined by PVT measurements and by weight. First stage AsF_5 intercalates were prepared by the procedure given in [6]. Fluorinations were carried out by treating $C_{10}AsF_5$ with F_2 at a pressure of 600 mm Hg for 12 to 20 h *in the same vessel*.

trans-N_2F_2

1 mmol N_2F_4 per 1 mmol intercalated AsF_5 is condensed on top of the blue graphite compound at -196°C *in the same vessel*. The vessel is allowed to warm up slowly and kept at room temperature for 1 to 2 days. N_2 is pumped off at -196°C and trans-N_2F_2 (90%) and NF_3 ($\leq$ 5%) are distilled from the solid at room temperature.

If necessary NF_3 can be separated by column chromatography [4].

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