

Reaction Ia has been reported,¹ and methyl-di-phenylsilyllithium, prepared from the disilane,⁸ was added to an ether solution of the (+)-chlorosilane and gave the (-)-disilane (*Anal. Calcd.*: C, 77.25; H, 8.30; Si, 14.45. *Found*: C, 77.40; H, 8.21; Si, 14.45) as a clear colorless liquid having $[\alpha]_D -5.03^\circ$ (*c* 6.3, benzene), in 82% yield after purification by chromatography over silica gel. In reaction sequence 2, a solution of (-)-disilane in tetrahydrofuran was added all at once to shiny lithium foil at 0° in an atmosphere of dry oxygen-free nitrogen. After 6 hr. of stirring the reactants, the solution of R_3Si^*Li in THF was syringed out of the flask and into a mixture of ether and dilute hydrochloric acid. Fractional distillation gave 50–60% yields of optically active neopentylphenylmethylsilane, R_3Si^*H .

Acknowledgment. We thank Dow Corning Corporation for continued generous support.

(8) H. Gilman and G. D. Lichtenwalter, *J. Am. Chem. Soc.*, **80**, 608 (1958).

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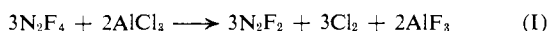
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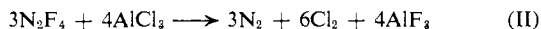
Preparation of *trans*-Difluorodiazine

Sir:

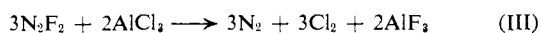
Pure *trans*-difluorodiazine can readily be prepared in about 45% yield from commercially available tetrafluorohydrazine and aluminum chloride.



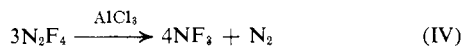
Reaction I is invariably accompanied by the formation of elementary nitrogen which accounts for the bulk of the N_2F_4 used.



The product N_2F_2 is also relatively slowly reduced by $AlCl_3$ to give elementary nitrogen and chlorine.



An additional undesirable reaction which may occur is the disproportionation of N_2F_4 to give nitrogen and NF_3 .



Reaction IV proceeds almost quantitatively at room temperature in the presence of trace quantities of $AlCl_3$.

Fortunately, both reactions III and IV can be inhibited effectively by adjusting conditions of temperature and pressure, respectively. Reaction III is extremely slow at -80° while reactions I, II, and IV are still quite rapid. The rate of disproportionation of N_2F_4 in the presence of $AlCl_3$ (reaction IV) is strongly pressure dependent, becoming almost negligible at pressures below 20 mm.

Consistent yields of 45–48% *trans*- N_2F_2 have been obtained from both batch and flow reactions involving

excess $AlCl_3$ and N_2F_4 at 15–20 mm. and -80° with contact times ranging from 0.5 to 5 min. Because of the necessarily low pressures, flow systems are strongly recommended.

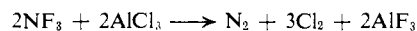
A convenient reactor can be prepared by subliming anhydrous $AlCl_3$ (15–20 g. for 30–50 mmoles of N_2F_4) onto the side-arm walls of a conventional Pyrex U-tube (16 mm. o.d.) by heating the material in the bottom of the vessel with a bunsen burner. It is necessary to activate the $AlCl_3$ before use by keeping it in contact with a small quantity of N_2F_4 at room temperature for 30 min. *Caution.* Do not use glass wool in the reaction tube as it may ignite.

The product is purified by washing with aqueous caustic soda followed by trap-to-trap vacuum distillation. Any unchanged N_2F_4 in the product can be destroyed by shaking it with water in the presence of elementary oxygen and a trace of nitric oxide. Concentrated nitric acid has also been used to remove N_2F_4 but this reagent should be avoided because of the danger of possible detonation. Samples of *trans*- N_2F_2 prepared in 48% yield in this laboratory contained approximately 0.2% NF_3 as the only impurity detectable in the infrared spectrum.

Observations made during the investigation of the above reactions indicate that at least two unstable solid NF -containing compounds are also formed in small amounts. Below -132° the activated $AlCl_3$ described above absorbs some N_2F_4 which cannot be pumped off. On warming, the solid liberates a mixture of N_2F_4 , *trans*- N_2F_2 , N_2 , and Cl_2 . Similarly, the reaction of N_2F_4 with $AlCl_3$ at -80° yields not only gaseous products but also a solid which slowly decomposes to give N_2 and Cl_2 at this temperature. In the presence of traces of moisture, N_2O is also formed in small amounts.

Additional work in this area is now in progress, including the study of reactions involving other metal salts and the nitrogen fluorides. Preliminary results indicate that $FeCl_3$ is similar to $AlCl_3$ in its action on N_2F_4 but the iron compound is considerably less reactive.

Contrary to an early report¹ by Ruff, NF_3 is also readily reduced to nitrogen by $AlCl_3$ at 70° .



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(1) O. Ruff, *Z. anorg. allgem. chem.*, **197**, 283 (1931).

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Electronic Spectra and Photochemistry of Adsorbed Organic Molecules. I. Spectra of Ketones on Silica Gel

Sir:

We have observed that silica gel-cyclohexane and silica gel-benzene matrices, if of sufficiently short path length, are highly transparent in the near-ultraviolet