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REACTION OF DIFLUORAMINE (HNF_2) WITH HYDRAZONES

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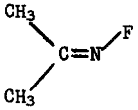
Difluoramine-induced fragmentation of 3,5,5-trimethylpyrazoline (1) prompted us to examine the reactions of HNF_2 with several acyclic hydrazones.

Exposure in a vacuum line of an excess of acetone phenylhydrazone (I) to HNF_2 resulted in a vigorous reaction producing N-fluorodimethylketimine (II), N_2, benzene, ammonium fluoride derivatives, and traces of acetone and N_2F_4.



II

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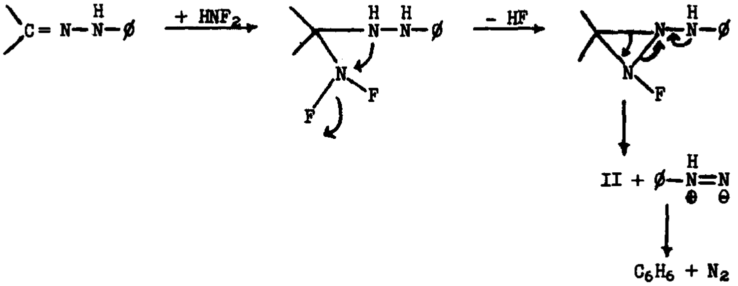
Compound II, obtained in 30-50% yield,[*] was isolated by vacuum line fractionation followed by gas phase chromatography over Silicone oil (Dow 710). The structure assignment follows from elemental analyses, the F^{19} n.m.r. spectrum which shows a single resonance at -25.6 ϕ (NF), the presence of bands in the infrared spectrum at 1670 cm^{-1} (C=N) and 890 cm^{-1} (NF), and the mass spectrum where mass numbers 15 (CH_3^+) and 41 (CH_3CN^+) are major peaks.

Formation of ketimine II from acetone phenylhydrazone and HNF_2 may be rationalized in several ways but a reasonable one consists of addition of HNF_2 to the C=N double bond (2) followed by intramolecular ring closure and fission (3).



When formaldehyde phenylhydrazone was treated with HNF_2 the major volatile products consisted of HCN, N_2, and benzene. Although no evidence for $H_2C{=}NF$ was obtained, this material is likely the precursor of HCN.

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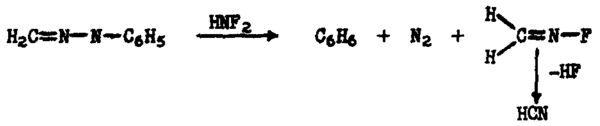
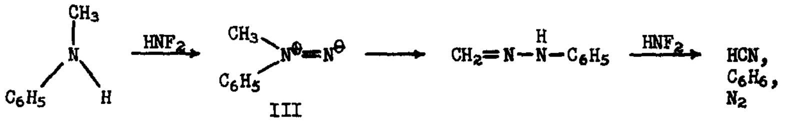
[*] Based on the equation $2\ I + HNF_2 \longrightarrow II + N_2 + C_6H_6 + I{\cdot}HF$



Interestingly, reaction of N-methylaniline with HNF_2 gave the same volatile products (HCN, N_2, benzene) as those obtained from formaldehyde phenylhydrazone, an observation consistent with the hydrazone intervening as an intermediate in the amine reaction. On the basis of previous work



(1,4) with secondary amines and HNF_2, we anticipated that N-methylaniline would be converted by HNF_2 to the diazene III and that this reactive intermediate could, by aryl migration and a hydrogen atom shift (5), give rise to formaldehyde phenylhydrazone.

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