

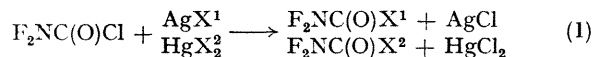
Reactions of Difluoroaminocarbonyl Chloride: An Improved Synthesis of Perfluorourea

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Summary Difluoroaminocarbonyl chloride undergoes metathesis with Ag^I or Hg^{II} pseudohalides; with the metal oxides, perfluorourea is formed quantitatively.

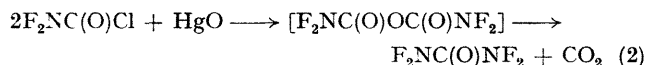
DURING an investigation of the chemistry of difluoroaminocarbonyl chloride,^{1,2} we find that reactions with Ag^I or Hg^{II} pseudohalides yield difluoroaminocarbonyl pseudohalides (reaction 1).



where X¹ = CN, NCO, NCS, N₃
X² = SCF₃, ON(CF₃)₂, N(CF₃)₂

When X is I or Br, little reaction occurs at 25°, and upon heating elemental halogen is formed. Reaction with silver trifluoroacetate quantitatively generates trifluoroacetic anhydride.

In addition, F₂NC(O)Cl will react with an excess of Ag₂O at 0° or with an excess of HgO at -78° to give CO₂ and F₂NC(O)NF₂ in nearly quantitative yield. It is likely that the perfluorourea is formed *via* decarboxylation of an unstable symmetrical anhydride (reaction 2). The only



published synthesis for perfluorourea involves a hazardous and tedious preparation which results in low yields accompanied by separation problems.^{1,3} Reactions at temperatures higher than those cited tend to result in formation of

difluoroaminocarbonyl fluoride⁴ at the expense of the perfluorourea. The condition of the solid surface and the reaction time are also important in obtaining optimum yields. Carbon dioxide formed as a by-product can be easily removed by fractional condensation, and difluoroamine by adsorption in 5 Å molecular sieves, leaving perfluorourea of high purity.

Characterisation of this pure material results in some additions and corrections to the previously published physical data. The carbonyl band is observed as a strong doublet at 1866—1859 cm⁻¹ which now brings NF₂C(O)NF₂ into line with other NF₂C(O)X compounds including the new ones mentioned above (doublet carbonyl stretch in 1905—1800 cm⁻¹ region). Additional bands are recorded in the far i.r. at 472w, 331m, and 255w. A 20 mole-% solution in CCl₃F yields only one broad resonance at -33.4 p.p.m. with respect to CCl₃F (*vs.* -30.8 with external reference), which under high resolution gives no indication of splitting by the nitrogen atom. In the u.v. range from 190—390 nm, an absorption maximum is observed at 202 nm. No molecular ion is detected in the mass spectrum at either 70 or 17 eV.

While pyrolysis of perfluorourea in Pyrex shows no decomposition below *ca.* 80°, pyrolysis in stainless steel results in decomposition to NF₂C(O)F and non-condensables at lower temperature due mainly to the fluorinating action of metal fluorides.

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