Central Research Laboratories, Minnesota Minning and Manufacturing Company

Organic Fluoronitrogens (1). I. The Direct Fluorination of Melon (2)

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The action of elemental fluorine upon the complex polyheterocycle, melon, yields products which contain 50% or more of fluorine and are solids or liquids of very low volatility. The structure assigned indicates essential retention of the tri-s-triazine structure, with addition of fluorine to most of the double bonds, replacement of hydrogen by fluorine, and a minor amount of cleavage of carbon-nitrogen bonds.

The direct fluorination of nitrogen compounds, that is, fluorination by reaction with elemental fluorine, has been studied in several laboratories. Among the compounds employed are hydrogen azide (3), potassium ferrocyanide and potassium ferricyanide (4), silver cyanide (5), hydrogen cyanide (6), cyanogen (6, 7), various other nitriles (8, 9, 10, 11, 12), several aliphatic and aromatic amines (6, 13, 14) pyridine and 2, 6-lutidine (15), cyanuric fluoride (16), perfluoroalkyl-s-triazines (17), several amides (9, 10), and methyl thiocyanate (10). Two of the reactions observed are replacement of hydrogen by fluorine and saturation of double bonds by fluorine. By means of these reactions, nitrogen heterocycles have been converted to their perfluorinated, saturated analogs, e.g., pyridine to $\overline{CF_2CF_2CF_2CF_2CF_2NF}$ and 2, 6-lutidine to the di-CF_3 analog (15), and cyanuric fluoride to $\overline{CF_2NFCF_2NFCF_2NF}$ (16).

Other reactions occurring in direct fluorination are cleavage of carbon-carbon and carbon-nitrogen bonds by fluorine and the formation of new carbon-carbon, carbon-nitrogen, and nitrogen-nitrogen bonds. Through such reactions there have been formed nitrogen heterocycles from non-heterocyclic precursors; examples of this are the formation of $\overline{CF_2NFCF_2NF}$ and $\overline{CF_2NFNFCF_2}$ from silver cyanide (5), $\overline{CF_2CF_2CF_2NFNF}$ from malononitrile (9), and $\overline{CF_2CF_2CF_2CF_2NF}$ from perfluorosuccinonitrile (11). The papers by Bigelow and his co-workers contain excellent discussions of the variety of reactions possible.

The fluorination products formed in the work summarized briefly above are gases or low-boiling liquids with relatively low contents of NF groups. Furthermore, bond cleavage and degradation have been so predominant, perhaps because of the relatively high temperatures frequently used in these fluorinations, as to result in low yields of perfluoroheterocyclic products. Here we wish to describe some solids and liquids of low volatility which contain notably higher amounts of NF groups and are obtained in very high yields. These have been prepared by direct fluorination of melon. Melon is a yellow solid, apparently first prepared by Berzelius and further described by Liebig (18); these early workers discovered the principal means of synthesis, which involve heating mercuric thiocyanate, "pseudothiocyanogen", melamine, or other s-triazine com-

pounds. The structure of melon has been shown by Redemann and Lucas (19) to be I in which the array of tri-s-triazine nuclei, represented by triangular symbols, may be of indefinite extent; a case has been described (19) in which, as judged from the hydrogen analysis, there were, on the average, approximately twenty-one of these nuclei per molecule of melon. Melon is thermally very stable, being unaffected by prolonged heating at 500°.

Melon was fluorinated in either of two ways. In the first procedure, fluorine, diluted with nitrogen, was passed over a thin layer of melon, held in a metal boat at room temperature. The product, a solid, could be removed directly from the boat. In the second method, the fluorine-nitrogen stream was bubbled through a suspension of melon in a fluorocarbon liquid (a mixture of perfluorooctanes). As fluorination proceeded the product dissolved in the fluorocarbon, from which it was ultimately recovered as a viscous liquid by evaporation of the fluorocarbon.
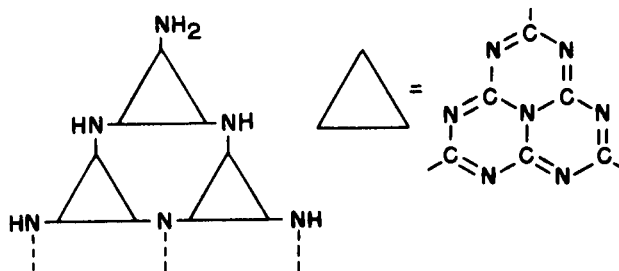
(I)
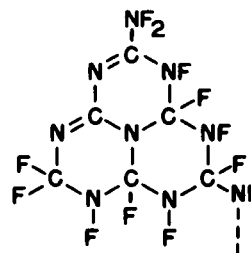
(II)

The products of the two methods are alike in that both are explosive and impact-sensitive and have essentially the same composition. They differ in that the liquid product is soluble in a variety of liquids and can therefore be characterized to a greater degree than the solid form, which is insoluble and has no definite melting point. The remainder of this discussion is devoted to the liquid product. It is a light yellow liquid, of honey-like consistency, which explodes violently when struck sharply. It is soluble in fluorotrichloromethane, acetone, ethyl acetate, benzene, chloroform, and other organic liquids. When ignited, it burns very rapidly with a light blue flame. It contains more than 50% fluorine and its molecular weight is about 700.

The infrared spectrum shows bands at 5.8 μ (assigned to C=N), 7.8 μ (unassigned), 7.5-9.4 μ (assigned to C-F), and 10-11 μ (assigned to N-F). Its nuclear magnetic resonance spectrum shows peaks at -20.6 $\phi*$ and -24.0 $\phi*$ (20) (assigned to NF_2 groups) and broad unresolved absorption in the range of +60 $\phi*$ to +100 $\phi*$ (assigned to ring CF_2 and NF) (21). The presence of unsaturation, indicated by the infrared spectrum, is confirmed by the relatively high refractive index which makes it evident that two or more double bonds, very likely conjugated, remain in each fluorinated tri-s-triazine nucleus. With these thoughts and the evidence afforded by elemental analyses and the n.m.r. spectrum, a tentative structure (II), which fits the observed facts, can be written for fluorinated melon. The positions of the double bonds may not always be as shown and the number of tri-s-triazine nuclei may vary from molecule to molecule (as it undoubtedly does in melon itself). It appears that the important reactions involved in the fluorination are addition of fluorine to double bonds and replacement of hydrogen by fluorine. Cleavage of carbon-nitrogen bonds also occurs but apparently to a smaller degree. There may be some opening of rings by this last reaction.

Fluorinated melon does not hydrolyze rapidly upon contact with water alone or even with sodium hydroxide solution. However, if enough acetone is added to the mixture with water to dissolve the fluorinated melon, hydrolysis occurs very rapidly upon titration with base. If this titration is of hydrofluoric acid, the amount of base consumed corresponds rather closely to the fluorine content of the fluorinated melon. This means that CF bonds, as well as NF bonds, are hydrolyzed. The hydrolysis

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of CF bonds is probably partly that of -C-F groups, formed by hydrolysis of -CF_2N=C= groups. Some fluorine attached to carbon is lost as HF eliminated from =CFNH- groups.

Fluorinated melon is strongly oxidizing toward potassium iodide. The product formed upon treatment with excess potassium iodide is a yellow solid resembling melon in its thermal stability. Its analyses indicate that this product contains much oxygen; its structure is unknown at present.

Preparation of Melon.

Fluffy form.

Mercuric thiocyanate was dried for several days under mercury vapor pump vacuum. It was then placed in a large evaporating dish and heated with a burner until it ignited. The product, a very voluminous yellow and black solid, was crushed lightly in a mortar and then heated under vacuum with gradually increasing temperature to remove the mercuric sulfide. The final heating, done at 500°, yielded a yellow, very fluffy solid.

Compact form.

Pseudothiocyanogen was prepared by a modification of the method described by Redemann and Lucas (19). A solution of potassium thiocyanate (1200 g., 12.3 moles) in water (2.5 l.) was stirred and held at about 60° in an ice bath while chlorine gas was bubbled into the mixture. When it appeared that no more solid was being formed the mixture was filtered and the filtrate was retreated with chlorine until formation of precipitate ceased. The solid obtained was washed with several portions of boiling water and dried to constant weight at 120°. The yield of dark orange solid (pseudothiocyanogen) was 540 g.

Anal. Found: C, 19.4; H, 1.3; N, 24.6; S, 50.7.

Pseudothiocyanogen was placed in a large evaporating dish and heated with a burner until it ignited. Heating was continued until the vapors no longer burned and the material possessed a uniform yellow color. It was transferred to an open flask and heated, with increasing temperature, until no more volatile matter was formed. This required over a week and the ultimate temperature reached was 500°. The product was a fine yellow powder.

Anal. Calcd. for an array of three tri-s-triazine nuclei: C, 35.8; H, 1.5; N, 62.8. Calcd. for the limiting form, C_6N_8: C, 39.1; H. 0; N, 60.9. Found: C, 35.0; H, 2.0; N, 61.2.

Fluorination of Melon.

Static bed method.

Fluffy melon (0.477 g.) was placed in a copper boat contained in a metal vessel and exposed at 25° to a stream of nitrogen containing 7.7% fluorine. After 0.037 mole of fluorine had passed into the vessel (1.6 hours), the reaction was terminated. The product was 0.652 g. of a yellow, crumbly solid which was impact-sensitive.

Anal. Found: F, 50.0; oxidizing power (toward KI), 20.7 meq. I^-/g.

Fluorocarbon suspension method.

Compact melon (3.00 g.) was suspended in a liquid mixture of perfluorooctanes (Minnesota Mining and Manufacturing Company) (175 ml.) contained in a Monel three-necked flask fitted with gas introduction tube, water-cooled reflux condenser, and thermocouple well. A stream of nitrogen was bubbled through the mixture. The fluorine content of the gas stream was gradually increased (over 4.6 hours) until pure fluorine was entering the mixture and 1.77 moles of fluorine had been used. The temperature of the reaction mixture was held at 24-36°. The mixture was filtered, yielding 1.32 g. of solid, and the filtrate was evaporated under reduced pressure. The liquid residue was dissolved in fluorotrichloromethane, filtered, and evaporated to constant weight at 25° under an ultimate pressure of 0.05 mm. The yield of yellow, viscous liquid was 3.62 g., n_D^{25}, 1.4315, d_4^{24}, 1.936.

Anal. Found: C, 17.4; F, 52.3; N, 30.4; mol. wt. (22), 710; oxidizing power (toward KI), 25.9 meq. I^-/g.

Reduction of Fluorinated Melon.

Fluorinated melon (0.30 g., 49% F, obtained by static-bed fluorination) was added in portions to a solution of potassium iodide (5 g.), water (5 ml.), and acetonitrile (40 g.). The mixture bubbled slightly and rapidly became very dark. After 1.5 hours the mixture was titrated to its end point with sodium thiosulfate solution and the finely divided solid was isolated by centrifuging. It was washed twice with water and dried *in vacuo*, yielding 0.10 g. of yellow solid. This material, heated on a metal spatula in a flame, did not melt until dull red heat was reached, when it changed color, liquefied, and was burned.

Anal. Found: C, 27.0; F, 2.0; N, 42.8.

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