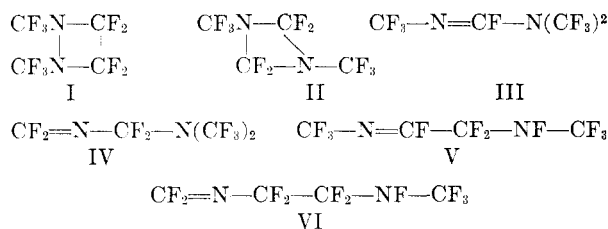


**Dimerization of Perfluoro-2-azapropene,
CF₃N=CF₂¹**

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Perfluoro-2-azapropene, CF₃N=CF₂,^{2,3} has been made to dimerize in 80% conversion and yield by ultraviolet irradiation in the presence of ethylene oxide.⁴ The analytically pure dimer C₄F₁₀N₂, b.p. 39°, can have six possible structures.



The presence of —CF=N— unsaturation is revealed in the non-complex infrared spectrum (expected of a chemical individual) by a very strong absorption at 5.66 μ. Thus the saturated cyclic dimers⁵ I and II are eliminated as possibilities or can at most be minor impurities. Furthermore, since CF₃—N=CF₂ has a strong band at 5.54 μ which is assigned to the N=C stretching vibration, structures IV and VI which also contain terminal —N=CF₂ groups and thus would be expected to have bands nearer 5.54 μ rather than at 5.66 μ, are very improbable. Structures III or V, therefore, remain as possibilities.

(1) The work herein reported was carried out under contract between the Office of Naval Research and the Pennsalt Chemicals Corp. Reproduction in whole or in part is permitted for any purpose of the United States Government.

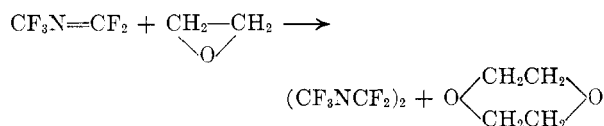
(2) D. A. Barr and R. N. Haszeldine, *J. Chem. Soc.*, 1881 (1955).

(3) J. A. Young, T. C. Simmons, and F. W. Hoffmann, *J. Am. Chem. Soc.*, **78**, 5637 (1956).

(4) Under these conditions, with CF₃CF=CF₂, where CF replaces N, copolymers with ethylene oxide are formed. See M. Hauptschein and J. M. Lesser, *J. Am. Chem. Soc.*, **78**, 676 (1956) for a description of the use of ethylene oxide in certain polymerizations of fluorinated olefins.

(5) These cyclic dimers may be considered the nitrogen analogs of the perfluoro(dimethylcyclobutanes) produced by the thermal dimerization of perfluoropropene. See M. Hauptschein, A. H. Fainberg, and M. Braid, *J. Am. Chem. Soc.*, in press.

It is also of considerable interest to note that the other principal product of this reaction was 1,4-dioxane, which is a dimer of ethylene oxide. Dimerization was not observed when either component was irradiated in the absence of the other under identical conditions. Thus the reaction is best represented by the equation:



EXPERIMENTAL

Pyrolysis of bis(trifluoromethyl)carbonyl fluoride. A modification of the procedure of Young *et al.*³ was used. The pyrolysis was carried out in a platinum-lined 1" O.D. nickel tube filled with CXA Columbia activated carbon (8 mesh). (CF₃)₂NCOF was passed through this tube heated at 490° ± 10° over a 26" length. The flow rate was 0.5–0.6 mole/hour. Conversions and yields of CF₃N=CF₂ and COF₂ were above 90%. At a temperature of 600° and a flow rate of 0.04 mole/hour only a very low yield of CF₃N=CF₂ was obtained; extensive decomposition of the azomethine must have taken place.

The dimerization of perfluoro-2-azapropene in the presence of ethylene oxide and ultraviolet light. Into a 90-ml. Pyrex glass ampoule 10.2 g. (0.767 mole) of CF₃N=CF₂ and 4.6 g. (0.104 mole) of ethylene oxide were introduced *in vacuo*. The sealed tube was exposed for 14 days to ultraviolet irradiation from a Hanovia SH burner. During this period the originally homogeneous solution separated into two layers. At the end of the reaction an amber colored upper layer represented about 40% of the total volume; the lower layer was colorless. The tube was opened at –78° and allowed to warm up to room temperature at atmospheric pressure. During this venting period no volatile products were collected in Dry Ice-cooled traps. Separation into two principal fractions was then accomplished by vacuum transfer at room temperature. The volatile, denser fraction on distillation in a small Vigreux unit gave 8 g. (78%) of a dimer, (CF₃NCF₂)₂, b.p. 39°, *n*_D²⁵ 1.27.

Anal. Calcd. for C₄F₁₀N₂: C, 18.1; F, 71.4; N, 10.5. Found: C, 18.1; F, 71.3; N, 10.2.

The less volatile fraction (*ca.* 7 g.) had a wide boiling range, *ca.* 30° (90 mm.) to >90° (0.1 mm.). Three grams of this fraction, b.p. 40–44° (93 mm.), consisted of at least 80% pure dioxane, as shown by its infrared spectrum.

In another experiment, 7.0 g. (0.053 mole) of CF₃N=CF₂ and 12.1 g. (0.28 mole) of ethylene oxide, sealed in a Vycor No. 7910 tube, were exposed to ultraviolet irradiation for 9 days. There were obtained (CF₃NCF₂)₂, in about 80% conversion and yield, and 1,4-dioxane, b.p. 99–101°; middle cut, b.p. 101°, f.p. 12°, *n*_D³⁰ 1.412, which was shown by its infrared spectrum to be at least 99% pure.

The principal infrared bands for C₄F₁₀N₂: 5.66, 7.18, 7.52, 7.89, 8.12, 8.38, 10.0, 12.05, 13.15, 13.37, 14.02, 15.23 μ.

PHILADELPHIA, PA.