The Photolysis of Perfluoro-2,3-diazabuta-1,3-diene

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WE recently described[1] the preparation of tetrafluoro-2,3-diazabuta-1,3-diene, $CF_2{:}N{\cdot}N{:}CF_2$ (I), and contrasted its thermal stability (it is stable up to 200°) with that of the hydrocarbon analogue which polymerises at room temperature.[2] A recent communication[3] reported spectroscopic evidence for the transient existence of the methylenimino-radical, $CH_2{:}N\cdot$, during the flash photolysis of 2,3-diazabuta-1,3-diene.

We have found that in the absence of co-reactants a gaseous sample of (I) is quantitatively converted to hexafluoro-2,4-diazapenta-1,4-diene, $CF_2{:}N{\cdot}CF_2{\cdot}N{:}CF_2$ (II), upon exposure to ultraviolet light (using quartz apparatus).

$$\underset{\text{(I)}}{3\,CF_2{:}N{\cdot}N{:}CF_2} \xrightarrow{h\nu} \underset{\text{(II)}}{2\,CF_2{:}N{\cdot}CF_2{\cdot}N{:}CF_2} + N_2$$

Hexafluoro-2,4-diazapenta-1,4-diene (II) is the first reported member of a series of perfluoro-$\alpha\omega$-bisazomethines and was characterised by its elemental analysis, infrared, mass, and ^{19}F n.m.r. spectra. The infrared spectrum shows a strong absorption at 5·62 μ corresponding to the $C{=}N$ stretching. The mass spectrum is in agreement with the proposed structure. The ^{19}F n.m.r. spectrum shows an AB pattern (J = 82 c./sec.) centred at 41·5 ϕ^*[4] corresponding to the $F_2C{:}N$ groups, and a broad unresolvable signal at 60·4 ϕ^* corresponding to $N{\cdot}CF_2{\cdot}N$.

The formation of the diazapentadiene (II) from the diazabutadiene (I) suggests that $CF_2{:}N{\cdot}N{:}CF_2$ decomposes into $CF_2{:}N\cdot$, $CF_2{:}$, and nitrogen. The absence of any detectable quantities of tetrafluoroethylene in the products indicates that $CF_2{:}N\cdot$ is formed more rapidly than difluorocarbene.

In the presence of fluoride ion, *e.g.*, as provided by cæsium fluoride, hexafluoro-2,4-diazapenta-1,4-diene (II) isomerises rapidly at room temperature to bis(trifluoromethyl)carbodi-imide (III).

$$\underset{\text{(II)}}{CF_2{:}N{\cdot}CF_2{\cdot}N{:}CF_2} \xrightarrow{F^-} \underset{\text{(III)}}{CF_3{\cdot}N{:}C{:}N{\cdot}CF_3}$$

Bis(trifluoromethyl)carbodi-imide is the first perfluorocarbodi-imide reported and was identified by its elemental analysis, infrared, mass, and ^{19}F n.m.r. spectra. The infrared spectrum shows a strong absorption at 4·52 μ assigned to the N:C:N stretching frequency and a weaker absorption at 6·64 μ assigned to the N:C:N bending. The mass spectrum is in agreement with the proposed structure. The ^{19}F n.m.r. spectrum shows a single peak at 50·2ϕ^* corresponding to the CF_3 groups.

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[1] R. A. Mitsch, *J. Heterocyclic Chem.*, 1964, **1**, 59; R. A. Mitsch and P. H. Ogden, *J. Org. Chem.*, 1966, **31**, 3833.

[2] N. P. Neureiter, *J. Amer. Chem. Soc.*, 1959, **81**, 2910.

[3] J. F. Ogilvie, *Proc. Chem. Soc.*, 1964, 359.

[4] G. Filipovich and G. V. D. Tiers, *J. Phys. Chem.*, 1959, **63**, 761.