

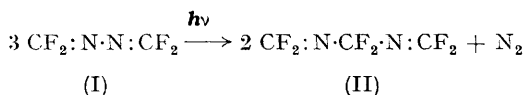
The Photolysis of Perfluoro-2,3-diazabuta-1,3-diene

By RONALD A. MITSCH and PAUL H. OGDEN

(Central Research Laboratories, Minnesota Mining and Manufacturing Co., St. Paul, Minnesota)

WE recently described¹ the preparation of tetrafluoro-2,3-diazabuta-1,3-diene, $\text{CF}_2:\text{N}\cdot\text{N}:\text{CF}_2$ (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 communication³ reported spectroscopic evidence for the transient existence of the methylenimino-radical, $\text{CH}_2:\text{N}\cdot$, during the flash photolysis of 2,3-diazabuta-1,3-diene.

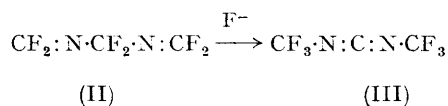
We have found that in the absence of co-reactants a gaseous sample of (I) is quantitatively converted to hexafluoro-2,4-diazapenta-1,4-diene, $\text{CF}_2:\text{N}\cdot\text{CF}_2\cdot\text{N}:\text{CF}_2$ (II), upon exposure to ultraviolet light (using quartz apparatus).



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 ¹⁹F 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 ¹⁹F n.m.r. spectrum shows an AB pattern ($J = 82$ c./sec.) centred at 41.5 ϕ^* corresponding to the $\text{F}_2\text{C}:\text{N}$ groups, and a broad unresolvable signal at 60.4 ϕ^* corresponding to $\text{N}\cdot\text{CF}_2\cdot\text{N}$.

The formation of the diazapentadiene (II) from the diazabutadiene (I) suggests that $\text{CF}_2:\text{N}\cdot\text{N}:\text{CF}_2$ decomposes into $\text{CF}_2:\text{N}\cdot$, $\text{CF}_2\cdot$, and nitrogen. The absence of any detectable quantities of tetrafluoroethylene in the products indicates that $\text{CF}_2:\text{N}\cdot$ is formed more rapidly than difluorocarbene.

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



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 4.52μ assigned to the N:C:N stretching frequency and a weaker absorption at 6.64μ 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 $50.2\phi^*$ corresponding to the CF_3 groups.

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