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STUDIES IN AZIDE CHEMISTRY. PART X [1]. SYNTHESIS OF PERFLUORO-2-AZIDO-1-AZACYCLOHEXENE

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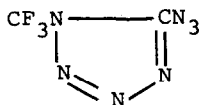
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## SUMMARY

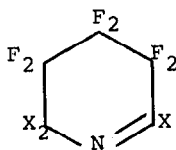
Perfluoro-2-azido-1-azacyclohexene can be prepared by treating perfluoro-1-azacyclohexene with an equimolar proportion of sodium azide (in acetonitrile) or azidotrimethylsilane under mild conditions;  $^{19}\text{F}$  n.m.r. analysis reveals that this new imidoyl azide participates in ring  $\rightleftharpoons$  chain valence tautomerism, the tetrazolo-isomer constituting 19% of the equilibrium mixture at 35 °C.

## INTRODUCTION

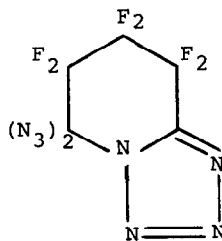
Our first experiments on nucleophilic azidation of fluorocarbon imines were carried out by McGlinchey [2] in the mid-1960s. He treated perfluoro-2-azapropene ( $\text{CF}_3\text{N}=\text{CF}_2$ ) with a two-molar proportion of sodium azide in acetonitrile at room temperature and isolated a crude product possessing an i.r. spectrum not inconsistent with the presence of



(I)



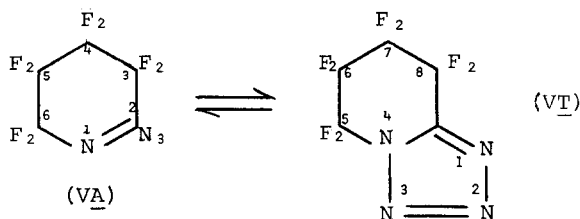
(II) X = F

(IV) X = N<sub>3</sub>

(III)

5-azido-1-trifluoromethyltetrazole (I);\* clinching evidence for the formation of this compound was not obtained because all the material available was lost in a violent explosion that occurred during distillation of the crude product. Similar azidation of perfluoro-1-azacyclohexene (II) with a ca. 2.5 molar proportion of sodium azide, followed by distillation of the product, afforded a liquid (b.p. 47 °C at ca. 3 mmHg) which was identified spectroscopically (i.r., <sup>19</sup>F n.m.r., and mass) as the tetrazole form (III) of the tri-azide (IV) associated with displacement of fluorine from both the C2 and C6 sites;\*\* unfortunately, a sample (12 mg) of this liquid detonated forcefully (the silica pyrolysis tube was shattered) when subjected to combustion analysis.

The occurrence of these explosions, coupled with McGlinchey's [2] observation that the bis(azido)tetrazole (III) appears to be formed even when perfluoro-1-azacyclohexene is treated with a deficiency of sodium azide, persuaded us to discontinue experimentation with fluoro-imines in 1967. Attempts to achieve controlled (i.e. mono-) azidation of perfluoro-1-azacyclohexene, now reported, were renewed in 1979 following work on the replacement of the imidoyl (C2) fluorine of perfluoro-1-azacyclohexene using trimethylsilanes  $\{(\text{II}) + \text{Me}_3\text{SiX} + \overline{\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{N}=\text{CX}} \text{ [X = Cl, ON}(\text{CF}_3)_2]\}$  [5,6].



\*Reaction of the conjugated bis-imine  $\text{CF}_3\text{N}=\text{CFCF}=\text{NCF}_3$  with sodium azide is claimed to yield the bis-tetrazole  $(\overline{\text{CF}_3\text{NN}=\text{NN}=\text{C}})_2$  [3].

\*\*The susceptibility of perfluoro-1-azacyclohexene to loss of fluorine as fluoride ion from both the C2 and C6 sites when under attack by an excess of a nucleophilic reagent is well known [4].

## DISCUSSION

Except for failure to effect an efficient product-from-solvent separation by simple distillation (this precluded determination of the yield), no problems were encountered during the synthesis of perfluoro-2-azido-1-azacyclohexene (VA) from perfluoro-1-azacyclohexene (II) via the 'silane route', and both spectroscopic (i.r.,  $^{19}\text{F}$  n.m.r., and mass) and elemental (C,F and N) analyses were performed without mishap. Experimentally, a ca. 4% excess (in terms of the molar ratio of reactants) of perfluoro-1-azacyclohexene was condensed into a cold ( $-196^\circ\text{C}$ ) evacuated vessel containing solvent (acetonitrile) and azidation agent (azidotrimethylsilane); after the mixture had warmed to room temperature, it was agitated for five days. The sample (b.p.  $60-63^\circ\text{C}$  at 120 mmHg) of perfluoro-2-azido-1-azacyclohexene (VA) isolated contained some (see below) of the tetrazolo-form (VT) and appeared not to be shock-sensitive.\* No explosion occurred when the azide was heated slowly to  $100^\circ\text{C}$  in an open test-tube, but droplets released from a pipette held ca. 15 cm above a steel plate heated to  $150-200^\circ\text{C}$  detonated immediately on contact with the hot surface. When subjected to flow pyrolysis in silica at  $250^\circ\text{C}$  and ca. 1 mmHg, the azide smoothly lost nitrogen and the organic products appeared in cold traps in the form of a white solid, thought to be polymeric in nature {m.p.  $> 200^\circ\text{C}$ ; insoluble in common solvents and Isceon 113 ( $\text{CF}_2\text{ClCFCl}_2$ ) or FC-43 [ $(\text{C}_4\text{F}_9)_3\text{N}$ ] and possessing the empirical formula  $\text{C}_5\text{F}_8\text{N}_2$  [5].

In subsequent work, the results of which belie McGlinchy's observation (single experiment) that multiple fluorine substitution occurs predominantly or even exclusively when perfluoro-1-azacyclohexene is treated with a deficiency of azide ion, perfluoro-2-azido-1-azacyclohexene was also prepared using sodium azide. Initially, small-scale experiments were carried out at low temperature (max.  $-10^\circ\text{C}$ )

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\* No explosion occurred when a sample enclosed in a thin-walled Pyrex ampoule at ambient temperature was struck with a cobbler's hammer.

between the inorganic azide suspended in acetonitrile or dichloromethane and a two-molar proportion of the fluoro-imine. These led to the adoption of a preparative procedure (giving 5 - 10 g of perfluoro-2-azido-1-azacyclohexene in ca. 65% yield) in which perfluoro-1-azacyclohexene was treated with a relatively small deficiency (5 - 10% in molar terms) of sodium azide in acetonitrile at ambient temperature (mixtures were warmed up from  $-196^{\circ}\text{C}$ ); isolation problems arising from the choice of solvent were overcome by employing perfluoropentane as an extractant for fluorocarbon material.

No attempt has been made to treat perfluoro-1-azacyclohexene with an excess of sodium azide, or to study the reaction of perfluoro-2-azido-1-azacyclohexene with sodium azide, and thereby to obtain further information on the product tentatively identified as the bis(azido)tetrazole (III) [2]. However, the  $\text{NaN}_3$ -technique employed to prepare perfluoro-2-azido-1-azacyclohexene has been used successfully to mono-azidate the fluorocarbon imines  $\text{CF}_3\text{N}=\text{CF}(\text{CF}_2)_n\text{CF}_3$ , where  $n = 0$  or 2 [ $\longrightarrow \text{CF}_3\text{N}=\text{C}(\text{N}_3)(\text{CF}_2)_n\text{CF}_3$ ] [5]; no problems were encountered in the azidoazahexene case ( $n = 2$ ), but a small sample (ca. 0.3 g) of its low-molecular-weight analogue ( $n = 0$ ) detonated violently whilst being transferred from a storage ampoule to a vacuum system after it had been analysed spectroscopically.

That perfluoro-2-azido-1-azacyclohexene (VA) exists in equilibrium with its fused-ring tautomer (VT) under normal conditions was deduced by n.m.r. analysis ( $^{19}\text{F}$ ) of the material obtained by mono-azidation of perfluoro-1-azacyclohexene; this product possessed the correct elemental composition (C, F and N values were determined) for a molecule  $\text{C}_5\text{F}_8\text{N}_4$ , and its mass spectrum - in which the prominent top-mass peak corresponded to  $\text{C}_5\text{F}_8\text{N}_2^{+}$  (i.e.  $\text{M}^{+} - \text{N}_2$  [cf. 7]) - was consistent with either tautomer. The intensities in the i.r. spectrum of the material of highly characteristic bands assignable to  $\text{N}_3$  and  $\text{C}=\text{N}$  (conjugated) functions indicated that the tetrazolo-form (VT) was present only as a minor constituent, if at all, in keeping with the generalization that azidoazomethine  $\longrightarrow$  tetrazole electrocyclization is disfavoured by the presence of electronegative substituents [8].

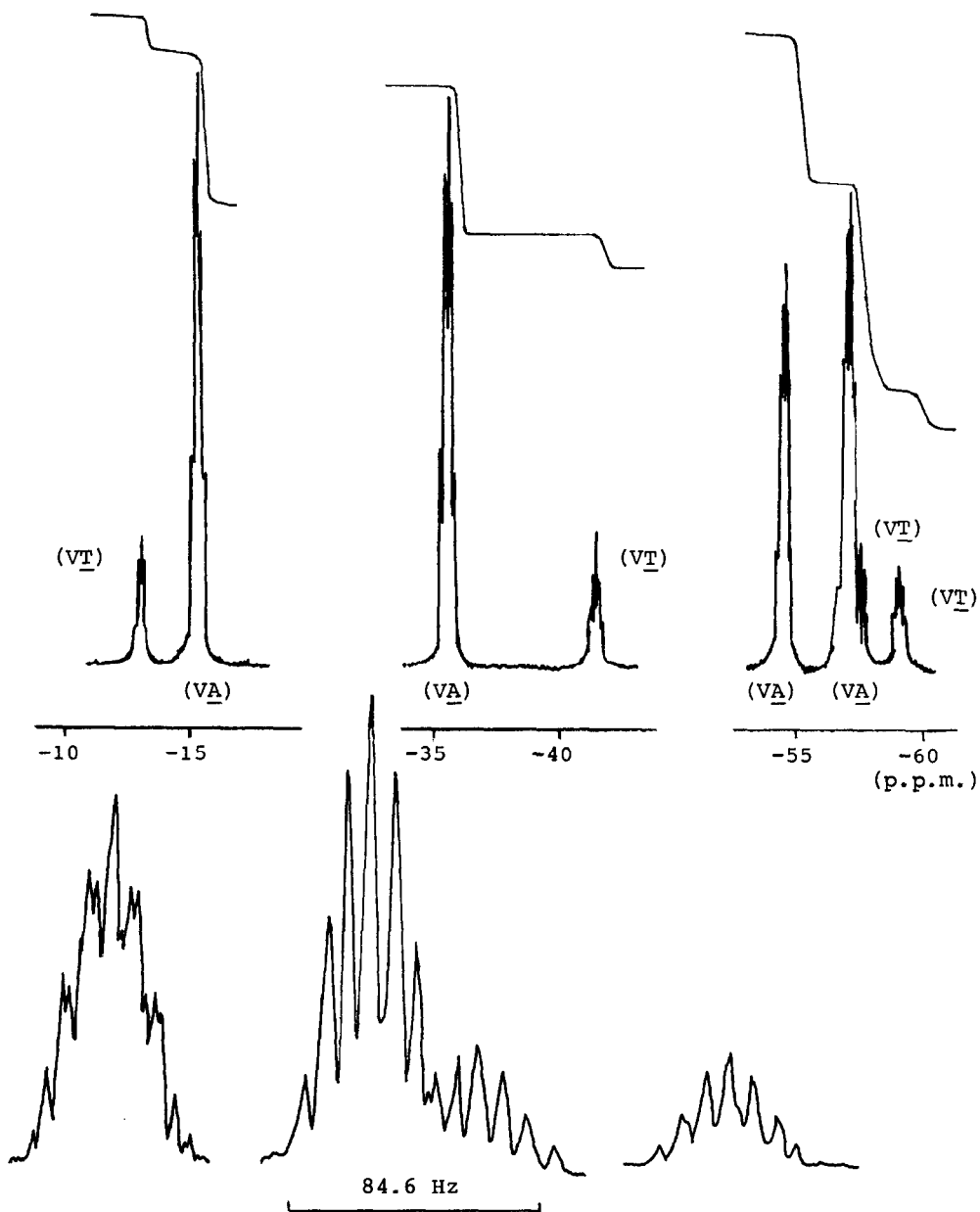


Figure. <sup>19</sup>F N.m.r. spectrum (84.6 MHz; 35 °C; no solvent; ext. TFA) of perfluoro-2-azido-1-azacyclohexene (VA) in equilibrium with perfluoro-5,6,7,8-tetrahydrotetrazolo[1,5-a]pyridine (VT) (upper trace: full spectrum; lower trace: -54 to -60 p.p.m., expanded scale).

$^{19}\text{F}$  N.m.r. analysis (see the Figure and the Experimental Section), however, clearly revealed the presence of two closely-related isomers, the major set of four absorptions fully characteristic of a 2-substituted octafluoro-1-azacyclohexene being accompanied by another set of four assignable to the tetrazolo-compound ( $\text{VT}$ ). From the integral trace (neat sample), the ratio ( $\text{VA}$ ):( $\text{VT}$ ) at 35 °C (probe temperature) was 4.3:1; addition of trifluoroacetic acid (ca. 60% v/v) to the sample shifted the equilibrium towards the azide side [ $\text{VA}$ ):( $\text{VT}$ ) = 9.1:1] - a phenomenon encountered with valence tautomerizations of this class in hydrocarbon chemistry [9].

#### EXPERIMENTAL

$^{19}\text{F}$  N.m.r. spectra were recorded at 84.6 MHz (ext.  $\text{CF}_3\text{CO}_2\text{H}$ ; chemical shifts to high field designated negative) using a Perkin-Elmer R32 instrument. Mass spectra were obtained with an AEI MS902 spectrometer (ionisation energy, 70 eV).

Perfluoro-1-azacyclohexene was prepared as described previously [4]. The usual precautions [10] were taken to minimise possible explosion damage during the synthesis and manipulation of perfluoro-2-azido-1-azacyclohexene.

#### Preparation of perfluoro-2-azido-1-azacyclohexene

##### (a) Using azidotrimethylsilane

Dry acetonitrile (10 cm<sup>3</sup>), perfluoro-1-azacyclohexene (4.94 g, 20.2 mmol), and azidotrimethylsilane (2.23 g, 19.4 mmol) were condensed separately into a cold (-196 °C) evacuated Pyrex tube (300 cm<sup>3</sup>) containing a PTFE-encapsulated magnetic stirrer follower. The tube was sealed (PTFE-glass Rotaflo valve) under vacuum and, after it had warmed to room temperature in an explosion-proof steel cabinet, was left with the stirrer in motion for 5 days. Subjection of the product to trap-to-trap fractional condensation, in vacuo, removed fluorotrimethylsilane (-196, mainly, and -78 °C traps) and some acetonitrile (-45 and -23 °C traps); distillation

at 120 mmHg in a one-piece semi-micro still of the distilland remaining in the 'stillpot trap' gave mixtures of acetonitrile and perfluoro-2-azido-1-azacyclohexene (examined by i.r. spectroscopy) and, finally, a fraction (0.50 g, 1.87 mmol, 10%), b.p. 60-63 °C (Found: C, 22.6; F, 56.7; N, 20.9. C<sub>5</sub>F<sub>8</sub>N<sub>4</sub> requires C, 22.4; F, 56.7; N, 20.9%),  $\lambda_{\text{max}}$  (film) 4.53, 4.60 (N<sub>3</sub> asym.str.), 6.06 (C=N str.)  $\mu\text{m}$ ,  $\underline{m/z}$  240 (top mass peak;  $\underline{M}^+$  - N<sub>2</sub>, 28%), 190 (C<sub>4</sub>F<sub>6</sub>N<sub>2</sub><sup>+</sup>, 89%), 138 (C<sub>4</sub>F<sub>4</sub>N<sup>+</sup>, 22%), 114 (C<sub>2</sub>F<sub>4</sub>N<sup>+</sup>, 30%), 100 (C<sub>2</sub>F<sub>4</sub><sup>+</sup>, 45%), 95 (C<sub>2</sub>F<sub>3</sub>N<sup>+</sup>, 87%), 69 (CF<sub>3</sub><sup>+</sup>, 100%), shown by <sup>19</sup>F n.m.r. spectroscopy (see the Figure) to be a 4.3:1 mixture of perfluoro-2-azido-1-azacyclohexene (VA; nc) [ $\delta_{\text{F}}$  -15.4 (6-CF<sub>2</sub>; quint.), -35.4 (3-CF<sub>2</sub>; mult.), -54.5 (4- or 5-CF<sub>2</sub>; mult.), -56.9 (5- or 4-CF<sub>2</sub>; sept.) p.p.m.] and perfluoro-5,6,7,8-tetrahydrotetrazolo[1,5-a]pyridine (VI; nc) [ $\delta_{\text{F}}$  -13.2 (5-CF<sub>2</sub>; quint.), -41.5 (8-CF<sub>2</sub>; quint.), -57.3 (6- or 7-CF<sub>2</sub>; sept.), -59.2 (7- or 6-CF<sub>2</sub>; 'sept.') p.p.m. {cf. [2] the compound believed to be perfluoro-5,5-bis(azido)-5,6,7,8-tetrahydrotetrazolo[1,5-a]pyridine (III),  $\delta_{\text{F}}$  -34.0 (quint.), -49.1 (quint.), -55.0 (t,t) p.p.m. (rel.int 1:1:1)}].

(b) Using sodium azide

Dry acetonitrile (15 cm<sup>3</sup>) and perfluoro-1-azacyclohexene (10.48 g, 42.7 mmol) were condensed, in vacuo, into a cold (-196 °C) Pyrex tube (200 cm<sup>3</sup>) containing dry sodium azide (2.61 g, 40.2 mmol) and a PTFE-coated magnetic stirrer follower. The tube was sealed (Rotaflo valve), placed in an explosion-proof steel cabinet and, after it had warmed to room temperature, left for 24 hours with the stirrer in motion. Volatile product was transferred in vacuo (the reaction vessel was heated gently using a hairdryer) to a cold (-196 °C) trap and, after it had warmed to room temperature, subjected to continuous extraction with perfluoro-pentane (b.p. 29 °C; ca. 175 cm<sup>3</sup>);\* distillation of the extract at atmospheric

\*This simple, mild technique for separating fluorocarbon-type material from acetonitrile was developed during work on perfluoro-N-chloropiperidine [11].

pressure using an adiabatic 10 x 1 cm column packed with Hastelloy Podbielniak spirals (to remove C<sub>5</sub>F<sub>12</sub>), followed by fractionation of the residue at 145 mmHg in a one-piece semi-micro Vigreux still, provided an equilibrium mixture (b.p. 63-65 °C) of perfluoro-2-azido-1-azacyclohexene and its tetrazolo isomer (6.91 g, 25.8 mmol, 64%), possessing the same spectroscopic (i.r., <sup>19</sup>F n.m.r., and mass) properties as the product isolated from the reaction of perfluoro-1-azacyclohexene with azidotrimethylsilane.

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