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STUDIES IN AZIDE CHEMISTRY. PART 11. THERMOLYSIS OF 4-AZIDOTETRAFLUOROPYRIDINE: EVIDENCE FOR THE OCCURRENCE OF A NITRENE-CARBENE REARRANGEMENT

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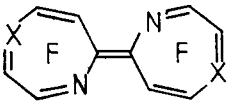
SUMMARY

Flow pyrolysis of vaporized 4-azidotetrafluoropyridine at 280-300 °C and atmospheric pressure in platinum gave dark-coloured intractable material containing trans-perfluoro[1,2-bis(pyrazinyl)ethene].

INTRODUCTION

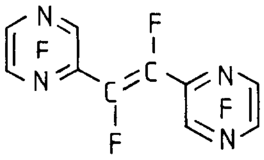
Vapour-phase flow pyrolysis of nitrogen-diluted azidopentafluorobenzene in platinum at 280-300 °C and *ca*. 760 mm Hg gives carbonaceous material from which perfluoro-2,7'-diaza-heptafulvalene (**1**) can be isolated (yield, 10%) [1,2]. Clearly, it was of interest to perform a similar experiment using 4-azidotetrafluoropyridine as feedstock.

RESULTS AND DISCUSSION



(**1**) X = CF

(**2**) X = N



(**3**)

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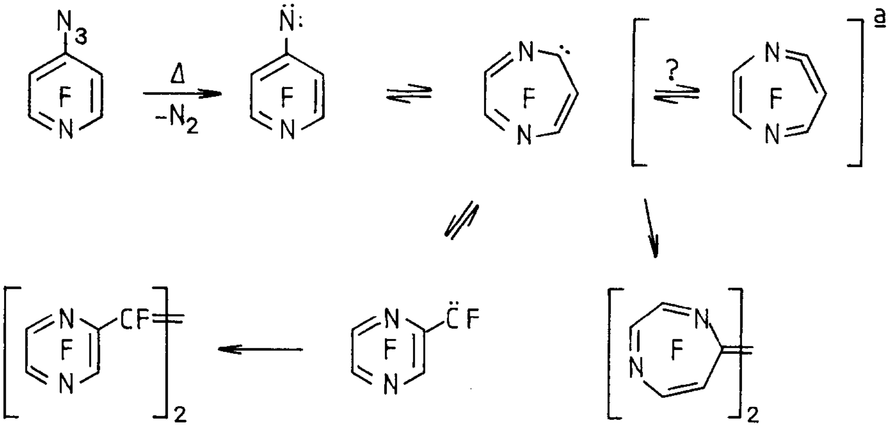
In a typical experiment, a slow stream of dry nitrogen was passed through warm (75-80 °C) 4-azidotetrafluoropyridine (10.0 g, 52 mmol) and thence through a hot (280-300 °C) platinum pipe (97 x 1 cm; electrically-heated length 56 cm) connected to two cold (-196 °C) traps until the supply of the azido-compound was exhausted (15 hr.). Nothing collected in the traps, and the product took the form of a dark brown solid adhering to the walls of the pyrolysis tube near the exit. This solid was scraped out and subjected to vacuum sublimation (bath temp. 140 °C ; *ca*.1 mmHg) to provide a pale-yellow solid (0.01 g, 0.3 mmol, 0.1%) (Found : C, 37.2; N, 16.4.Calc. for $C_5F_4N_2$: C, 36.6; N, 17.1%), m.p. 170-174 °C, which was shown by mass spectrometry to be a dimer of tetrafluoro-4-pyridylnitrene [*m*|*z* 328 ($C_{10}F_8N_4^{+\cdot}$, 100%), 309 ($M^{+\cdot}-F^{\cdot}$,77%); 70 eV electron beam ionisation energy]. ^{19}F N.m.r. analysis (see below) revealed immediately that this dimer was not a tetra-azaheptafulvalene (**2**), *i.e*. the expected product by analogy with the formation of the corresponding diaza-compound (**1**) from azidopentafluorobenzene under the same conditions [2], but *trans*-perfluoro[1,2-bis(pyrazinyl)ethene] (**3**). The sublimation residue (Found : C, 39.2 ; H, 0.3 ; F, 26.9 ; N, 17.8%) did not melt below 360 °C and gave an i.r. spectrum comprised of broad, diffuse absorptions.

Formation of perfluoro[1,2-bis(pyrazinyl)ethene](**3**) can be accommodated in terms of a Crow-Wentrup [3] nitrene $\rightleftharpoons$ carbene interconversion sequence (see the Scheme) which was used previously to rationalise the formation of tetrafluoropyrazine via pyrolysis of 4-(dichloroamino)tetrafluoropyridine [4]; naturally (*cf*. [1]), the Scheme allows for the formation of perfluoro-2,4',5,7'-tetra-azaheptafulvalene (**2**),so should an opportunity arise, we intend to investigate further the thermal decompositions of 4-azidotetrafluoropyridine and azidopentafluorobenzene to throw light on the mechanistic situation. The failure to obtain a heptafulvalene derivative from 4-azidotetrafluoropyridine means that formation of compound (**1**) in the case of azidopentafluorobenzene [1,2] is still unique, whereas production of the ethylenic dimer (**3**) finds analogy in the formation of small amounts (1-3% yield) of 1,2-bis(2-pyridyl)ethenes in thermolytic reactions designed to probe phenylnitrene $\rightleftharpoons$ 2-pyridylcarbene interconversions of the hydrocarbon class [3,5].



(3) (2)

SCHEME

[a] Cf. ref.[1]

The ^{19}F n.m.r. spectrum of the new pyrazinylethene (3) (measured in $CDCl_3$ at 75.29 MHz on a Bruker WP80 instrument) showed four absorption bands of equal intensity at (external CF_3CO_2H ref.) 3.3 (d x t x d; F-3; $|J_{3,6}|$ = 42.1, $|J_{3,7}+J_{3,7'}|$ = 47.0, $|J_{3,5}|$ = 6.9 Hz, -3.2 (d x d; F-5; $|J_{5,6}|$ = 20.2 Hz), -11.9 (d x d; F-6), and -67.7 p.p.m. (t; F-7). The large magnitude of J_{36} is quite characteristic of fluoropyrazines [6], and the other coupling constants of ring fluorines fall within the usual ranges. The coupling to the ethene fluorines (F-7), which is of the 'deceptively simple' A_2X_2-type, is presumably dominated by $J_{3,7}$ and reflects a through-space contribution. The chemical shifts of the ring fluorines are similar to those observed in perfluoro-(2-alkylpyrazines) [7], and, overall, the spectrum is entirely consistent with structure (3).

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