

Received October 5, 1989; accepted January 31, 1990

STUDIES IN AZIDE CHEMISTRY. PART 14 [1]. THERMOLYSIS OF PERFLUORO-4-AZIDOPYRIDINE AND PERFLUORO-4-AZIDOTOLUENE IN THE PRESENCE OF PENTA- AND HEXA-METHYLBENZENE

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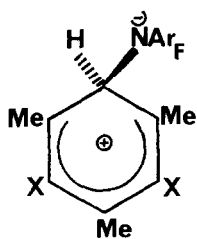
SUMMARY

Thermolysis of perfluoro-4-azidopyridine and perfluoro-4-azidotoluene in the presence of a large excess (10 molar) of pentamethylbenzene gave mainly (>60%) products expected from nitrene 'insertions' at the nuclear C-H bond, *i.e.* $\text{Ar}_\text{F}\text{NHC}_6\text{Me}_5$ ($\text{Ar}_\text{F} = 4\text{-C}_5\text{F}_4\text{N}$, $4\text{-C}_6\text{F}_4\text{CF}_3$). Similar decomposition of perfluoro-4-azidotoluene in hexamethylbenzene gave a complex mixture containing perfluoro-p-toluidine.

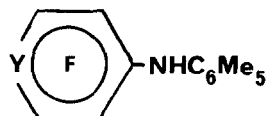
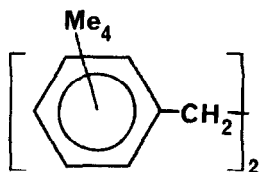
INTRODUCTION

Previously, we reported that mesitylene (1,3,5-trimethylbenzene) acts as a powerful 'trap' for putative singlet nitrenes generated thermally (170 °C) from perfluoro-4-azidopyridine and its tolyl analogue [1]. Formation of the diarylamines isolated, $4\text{-(2,4,6-Me}_3\text{C}_6\text{H}_2\text{NH)C}_5\text{F}_4\text{N}$ and $4\text{-(2,4,6-Me}_3\text{C}_6\text{H}_2\text{NH)C}_6\text{F}_4\text{CF}_3$, was explained on the basis of initial production of dipolar σ -complexes (A ; $\text{X} = \text{H}$). We have now determined the effect of replacing the mesitylene by its penta- and hexa-methyl counterparts, neither of which seem to have been used in any nitrene trapping studies before.

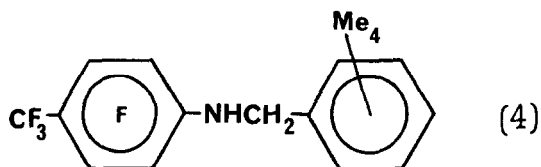
RESULTS AND DISCUSSION



(A)

(1) $Y = N$ (3) $Y = CCF_3$ 

(2)



(4)

Liquid-phase thermolysis (178 °C for 5 h) of 4-azidotetrafluoropyridine in the presence of a large excess of pentamethylbenzene (azide:trap ratio = 1:10 molar), under nitrogen, yielded a complex brown solid from which only 2,3,5,6-tetrafluoro-4-(pentamethylphenylamino)pyridine(1) and material believed to be impure 1,2-bis-

(tetramethylphenyl)ethane (2) (isomeric composition not determined) were isolated, the yields being 60 and <1% respectively. A similar experiment with the carbocyclic azide perfluoro-4-azidotoluene also provided mainly the product of notional insertion of the corresponding nitrene into the nuclear C-H bond of pentamethylbenzene, namely heptafluoro-4-(pentamethylphenylamino)-toluene (3; 65%, isolated material); also isolated was a trace (<1% yield) of material comprising two isomers (ratio 1:3 by ^{19}F n.m.r. analysis) of N-[2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl]-tetramethylbenzylamine (4), i.e. the expected product of 'insertion' into side-chain C-H. 1,2-Bis(tetramethylphenyl)ethane (2) was shown to be present in the crude product but was not isolated.

Even more complex mixtures were obtained when perfluoro-4-azidotoluene was heated (170 °C) under nitrogen with hexamethylbenzene; azide:trap ratios of both 1:10 and 1:1 were used in this case to make easier the recovery of product mixtures for chromatographic and spectroscopic analysis (C_6Me_6 melts at 166-7 °C and boils at 265 °C). The sole product identified (HPLC) was perfluoro-p-toluidine.

The yields of isolated products presumed to be formed via attack of singlet tetrafluoro-4-pyridylnitrene ($\rightarrow$ 1, 60%) or heptafluoro-4-tolynitrene ($\rightarrow$ 3 65%) on pentamethylbenzene to give σ -complex A (X = Me) initially are almost the same as those of the analogous amino-compounds obtained using 1,3,5-trimethylbenzene as the trap under nearly identical conditions. Seemingly, the reduced probability for attack at a ring CH position on changing from *sym*-trimethyl- to pentamethyl-benzene, coupled with the extra steric hindrance (buttressing effect) caused by the other two methyl substituents, is offset by the greater susceptibility towards electrophilic attack [4] shown by the pentamethylated benzene. The formation of 1,2-bis(tetramethylphenyl)ethane (2) in the reactions with each of the azides is believed to arise from intersystem crossing of singlet nitrenes to their triplet counterparts; this would also account for the production of the benzylamine derivative 4 ($4\text{-CF}_3\text{C}_6\text{F}_4\dot{\text{N}} + \text{C}_6\text{HMe}_5 \rightarrow 4\text{-CF}_3\text{C}_6\text{F}_4\dot{\text{N}}\text{H} + \text{C}_6\text{HMe}_4\text{CH}_2\cdot \rightarrow 4\text{-CF}_3\text{C}_6\text{F}_4\text{NHCH}_2\text{C}_6\text{HMe}_4$), whose analogue may have gone undetected in the experiment involving perfluoro-4-azidopyridine. Note, however, that while no such

circumstantial evidence was found for triplet species in the previous studies [1] involving 1,3,5-trimethylbenzene as a trap for tetrafluoro-4-pyridylnitrene or its tolyl analogue, both 1,2-bis(3,5-dimethylphenyl)ethane (corresponding to 2) and 4-amino-3-chlorotrifluoropyridine or 4-amino-3,5-dichlorodifluoropyridine were formed as byproducts when 4-azido-3-chlorotrifluoropyridine or 4-azido-3,5-dichlorodifluoropyridine were thermolyzed in that trapping agent. Incursion of triplet nitrenes in the cases of these chloro-azides was also ascribed, in part, to steric effects [1].

Presumably, the perfluoro-p-toluidine detected amongst the numerous products formed when perfluoro-4-azidotoluene was thermolysed in hexamethylbenzene arose through the incursion of triplet perfluoro-4-tolylnitrene [$4\text{-CF}_3\text{C}_6\text{F}_4\dot{\text{N}} + \text{C}_6\text{Me}_6 \rightarrow \text{C}_6\text{Me}_5\text{CH}_2\cdot + 4\text{-CF}_3\text{C}_6\text{F}_4\dot{\text{N}}\text{H} \rightarrow (\text{with } \text{C}_6\text{Me}_6) 4\text{-CF}_3\text{C}_6\text{F}_4\text{NH}_2$]. Neither this amine nor 4-aminotetrafluoropyridine were detected in the crude products from the azide pyrolyses carried out in pentamethylbenzene.

EXPERIMENTAL

General Remarks

Reference 1 contains details of the procedure employed to study the thermal decomposition of azides in aromatic substrates, and of the analytical techniques employed. Perfluoro-4-azidopyridine and perfluoro-4-azidotoluene were prepared as described by Banks et al. [2,3].

Trapping Experiments Involving Pentamethylbenzene

(a) With perfluoro-4-azidopyridine

Perfluoro 4-azidopyridine (2.0 g, 10.4 mmol) and pentamethylbenzene (15.4 g, 104.0 mmol) were heated together for 5 hours under nitrogen at 178 °C [the magnetic stirrer was switched on once the pentamethylbenzene had melted (50-51 °C)]. Vacuum distillation of the brown product to remove pentamethylbenzene (ca. 11 g), followed by vacuum sublimation of the 6-component (by HPLC analysis) crystalline brown stillpot residue, gave a yellow solid. Recrystallization (twice) of this sublimate from aqueous ethanol provided white 2,3,5,6-tetrafluoro-4-(pentamethylphenylamino)-

pyridine (1) (nc) (1.96 g, 6.28 mmol, 60%) [Found : C, 62.2; H, 5.0; F, 24.1; N, 8.6%; M^+ , 312 (base peak). $C_{16}H_{16}F_4N_2$ requires C, 61.5; H, 5.1; F, 24.4; N, 9.0%; M , 312], m.p. 148-150 °C, λ_{max} (KBr disc) 2.98 μ m (N-H str.), δ_F (in $CDCl_3$) -15.5 (m; 2-,6-F) and -86.0 (m; 3-,5-F) p.p.m., δ_H (same soln.) 2.15, 2.20 (overlapping singlets; 5 x CH_3), 5.9 (br.s; NH) p.p.m. Evaporation of the mother liquor provided a 3-component (by TLC and HPLC analysis) yellowish solid containing pentamethylbenzene; recrystallization of this material from aqueous ethanol gave a white solid thought to be 1,2-bis(tetramethylphenyl)ethane (2) (0.01 g, 0.03 mol, 0.3%) (Found: C, 86.2; H, 10.3%; M^+ , 294. Calc. for $C_{22}H_{30}$: C, 89.8; H, 10.2%; M , 294), m.p. 179-180 °C, m/z 294 ($C_{22}H_{30}^+$, rel.abund. 53%), 160 ($C_{12}H_{16}^+$, 100%), 147 ($C_{11}H_{15}^+$, 24%), δ_H (in $CDCl_3$) 2.1-2.5 (c; 8 x CH_3), 3.9 (s; 2 x CH_2), and 6.3 (2 x aromatic CH) p.p.m., despite the poor carbon analysis.

(b) with perfluoro-4-azidotoluene

Experiment (a) was repeated at 160 °C, using perfluoro-4-azidotoluene (2.0 g, 7.7 mmol) as the nitrene source. Vacuum sublimation of the distillation residue following removal of the excess of pentamethylbenzene gave a 4-component yellow solid which could not be resolved into its components by semi-preparative scale HPLC. Recrystallisation of the mixture from aqueous ethanol (twice) provided impure (by elemental analysis) white needles (m.p. 140-144 °C) of heptafluoro-4-(pentamethylphenylamino)toluene (3) (nc) (1.9 g, 5.0 mmol, 65%) [Found: C, 58.2; H, 4.5; N, 3.5%; M^+ , 379 (base peak). $C_{18}H_{16}F_7N$ requires C, 57.0; H, 4.2; N, 3.7%; M , 379], λ_{max} (mull) 2.94 μ m (N-H str.), δ_F (in $CDCl_3$) +23.7 (t, J 21 Hz; CF_3), -65.0 (m; 2-,6-F), -83.0 (m; 3-,5-F) p.p.m., δ_H (same soln.) 2.20, 2.24 (overlapping singlets; 5 x CH_3) and 5.55 (vbr.s; NH) p.p.m. Evaporation of the mother liquor and further recrystallization of the residue from aqueous ethanol provided yellow needles (m.p. 112-126 °C) of a mixture of N -[2,3,5,6-tetrafluoro-4-(trifluoromethyl)-phenyl]tetramethylbenzylamines (4) (0.1 g, 0.3 mmol, 0.4%) [Found: C, 57.3; H, 4.3; F, 34.7; N, 3.6%; M^+ , 379. $C_{18}H_{16}F_7N$ requires C, 57.0; H, 4.2; F, 35.1; N, 3.7%; M , 379], λ_{max} (mull) 2.98 μ m (N-H str.), δ_F (in $CDCl_3$) +23.4 (two closely overlapping 22 Hz triplets of unequal intensity; CF_3), -65.0 (mult; 3-,5-F), -81.8 and -83.2 (two mult., rel.int. 1:3; 2-,6-F in both cases) p.p.m., δ_H (same soln.)

2.28 (br.s; 4 x CH₃), 4.63 and 4.71 (br. overlapping s; CH₂ groups), 5.65 (vbr.s; NH), and 7.05, 7.69 (br. overlapping s; aromatic CH groups) p.p.m., m/z 379 (M^+ , 33%), 147 (Me₄C₆HCH₂⁺, 100%). ¹H N.m.r. and HPLC examination of the residue before the final recrystallization revealed the presence of 1,2-bis(tetramethylphenyl)ethane (2), as found in experiment (a) above with perfluoro-4-azidopyridine.

Thermolysis of Perfluoro-4-azidotoluene in Hexamethylbenzene

The azide (6.0 g, 23.2 mmol) was added dropwise during 45 minutes to hexamethylbenzene (3.7 g, 22.8 mmol) held at 170 °C under nitrogen. After the reaction mixture had been heated for a further 4 hours, it was cooled and (now brown in colour) subjected to DCFC (eluant : petroleum ether, b.p. 40-60 °C). A yellow fraction was collected which proved to be a complex mixture (at least ten components plus hexamethylbenzene) when examined by analytical HPLC. One of the components was identified as perfluoro-p-toluidine by comparison of its retention time with that of an authentic sample.

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