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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. $Ar_FNHC_6Me_5$ (Ar_F = 4-C_5F_4N, 4-$C_6F_4CF_3$). 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-(2,4,6-$Me_3C_6H_2NH)C_5F_4N$ and 4-(2,4,6-$Me_3C_6H_2NH)C_6F_4CF_3$, was explained on the basis of initial production of dipolar σ-complexes (**A**; X = 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.

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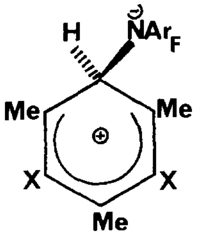
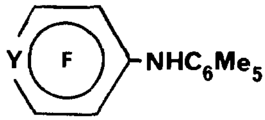
RESULTS AND DISCUSSION

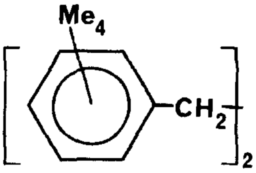


(A)

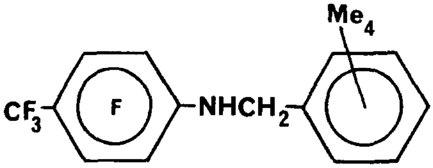


(1) Y = N

(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 (→ **1**, 60%) or heptafluoro-4-tolylnitrene (→ **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** ($4\text{-}CF_3C_6F_4\dot{N}\cdot + C_6HMe_5 \rightarrow 4\text{-}CF_3C_6F_4\dot{N}H + C_6HMe_4CH_2\cdot \rightarrow 4\text{-}CF_3C_6F_4NHCH_2C_6HMe_4$), 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 [$4\text{-}CF_3C_6F_4\dot{N}\cdot + C_6Me_6 \rightarrow C_6Me_5CH_2\cdot + 4\text{-}CF_3C_6F_4\dot{N}H \rightarrow$ (with C_6Me_6) $4\text{-}CF_3C_6F_4NH_2$]. 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). $C_{16}H_{16}F_{4}N_{2}$ requires C, 61.5; H, 5.1; F, 24.4; N, 9.0%; M, 312], m.p. 148-150 °C, $\lambda_{max.}$ (KBr disc) 2.98 µm (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). $C_{18}H_{16}F_{7}N$ requires C, 57.0; H, 4.2; N, 3.7%; M, 379], λ_{max} (mull) 2.94 µm (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. $C_{18}H_{16}F_{7}N$ requires C, 57.0; H, 4.2; F, 35.1; N, 3.7%; M, 379], λ_{max} (mull) 2.98 µm (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 CH_3), 4.63 and 4.71 (br. overlapping s; CH_2 groups), 5.65 (vbr.s; NH), and 7.05, 7.69 (br.overlapping s; aromatic CH groups) p.p.m., *m/z* 379 ($\underline{M}^+$, 33%), 147 ($Me_4C_6HCH_2^+$, 100%). ^{1}H 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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