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STUDIES IN AZIDE CHEMISTRY. PART 12. ONE-POT CONVERSION OF 4-AZIDOTETRAFLUOROPYRIDINE TO 1,3,4-TRIFLUORO-7,9-DIMETHYL-11H-PYRIDO[4,3-c]BENZO[1,2]DIAZEPINE

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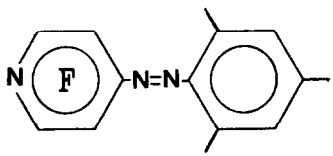
SUMMARY

Thermolysis of 4-azidotetrafluoropyridine in the presence of an excess of mesidine at 170 °C yields tetrafluoro-4-(2,4,6-trimethylphenylazo)-pyridine, which undergoes intramolecular dehydrofluorination *in situ* to provide 1,3,4-trifluoro-7,9-dimethyl-11H-pyrido[4,3-c]benzo[1,2]diazepine.

INTRODUCTION

The discovery described here stemmed from utilisation of the well-established thermal behaviour of 4-azidotetrafluoropyridine [1] in a search for high-temperature nitrene traps suitable for probing the mechanism of the pyrolytic rearrangement of perfluoro-(6-azido-2,6-dimethyl-1-azacyclohexene) [2]. As explained recently [3], it was made shortly after Alty [4] had



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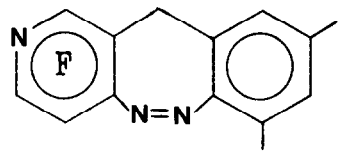

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stumbled across the acetic acid-catalysed conversion of tetrafluoro-4-(2,4,6-trimethylphenylazo)pyridine (1) to 1,3,4-trifluoro-7,9-dimethyl-11H-pyrido[4,3-c]benzo[1,2]diazepine (2) and hence deserves attention as an unusual case of carbon-copy serendipity in the same laboratory.

RESULTS AND DISCUSSION

Aniline [5], p-fluoroaniline [5], or pentafluoroaniline [5,6,7] have been used successfully to provide circumstantial evidence for nitrenic decomposition of azidopentafluorobenzene, perfluoro-4-azidotoluene, 4-azidotetrafluoropyridine and 4-azido-3-chlorotrifluoropyridine at temperatures in the range 130-165 °C. Pentafluoroaniline was the 'cleanest', most efficient (yield-wise) trap, and importantly no secondary reactions involving nucleophilic displacement of fluorine from pentafluorophenylazo-compounds formed initially *via* nitrene insertion into N-H bonds was detected. Attention was turned to mesidine (2-amino-1,3,5-trimethylbenzene, b.p. 233 °C) as a trap for tetrafluoro-4-pyridylnitrene after it had been discovered that (i) this arylamine does not readily displace fluorine from pentafluoropyridine, and (ii) the corresponding hydrocarbon, mesitylene (b.p 165 °C), is a good trap for the nitrene, insertion into ring C-H occurring to the exclusion of attack on the methyl C-H bonds [8].

Thus, 4-azidotetrafluoropyridine (2.0 g, 10.4 mmol) and freshly-distilled mesidine (14.0 g, 104 mmol) were heated together at 175 °C under an atomosphere of nitrogen for 5 hours. The product was poured into water (*ca.* 100 cm^3) and organic material was extracted with diethyl ether (3 x 200 cm^3);the ether extracts were then concentrated (to *ca.*100 cm^3) and, after being shaken with 2M-hydrochloric acid (2 x 100 cm^3), washed with water, dried overnight ($MgSO_4$), and subjected to dry-column flash chromatography on silica (Merck GF_{254}, Art. 7730) eluted with dichloromethane-petroleum ether (b.p. 40-60 °C) (3:2 v/v). This provided tetrafluoro-4-(2,4,6-trimethylphenylazo)pyridine (1) (0.8 g, 2.7 mmol, 26%), 1,3,4-trifluoro-7,9-dimethyl-11H-pyrido[4,3-c]benzo[1,2]diazepine (2) (0.3 g, 1.1 mmol, 10%), and 4-aminotetrafluoropyridine (4% yield), each of which was identified spectroscopically, using authentic samples for comparison. HPLC Analysis of the crude reaction product revealed the presence of numerous compounds, each in small amount. When the

reaction was repeated at 160 °C for 14 hours, the complex reaction product was found to contain no tetrafluoro-4-(2,4,6-trimethylphenylazo)pyridine (1) and the yield of the diazepine (2) isolated was 30%. That the diazepine is slowly destroyed when heated in mesidine was established by heating a dilute solution (ca. 0.25 molar) of the former in the latter at 175 °C for 6 hours under nitrogen; only 70% of the diazepine was recovered from the tarry material formed. Since the limit of this one-pot azide route to the novel diazepine (2) was 30% in our hands, the method is not as efficient as Alty's method [4], which provides the required compound in at least 65% overall yield starting from commercial pentafluoropyridine if one is able to carry out the diazotisation/coupling to mesitylene [⟶ (1)] of 4-aminotetrafluoropyridine in anhydrous hydrogen fluoride; the yield falls to ca. 50% if concentrated sulphuric acid [9] is utilised in the diazotisation procedure. The azide-route yield, based on pentafluoropyridine, is only ca. 20%.

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