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PRELIMINARY NOTE

Tetrafluoro-4-nitrosopyridine

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SUMMARY

2,3,5,6-Tetrafluoro-4-nitrosopyridine has been synthesised via oxidation of 4-amino-2,3,5,6-tetrafluoropyridine with peroxytrifluoroacetic acid in dichloromethane. It reacts with diphenyldiazomethane in light petroleum to give, inter alia, C,C-diphenyl-N-(tetrafluoro-4-pyridyl)nitrone.

Simple nucleophilic substitution of fluorine in pentafluoropyridine has provided the key to the synthesis of a veritable host of 4-substituted tetrafluoropyridines since the parent molecule was first prepared nearly thirty years ago [1]. To our knowledge, however,

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the relatively simple compound tetrafluoro-4-nitrosopyridine has not been reported, despite its potential as a source of interesting chemistry and a fairly obvious promising means of synthesis, namely oxidation of the readily-procured 4-aminotetrafluoropyridine[+] (*cf.* the per-acid oxidation of $C_6F_5NH_2$ to C_6F_5NO [2]).

In fact, dropwise addition of 4-aminotetrafluoropyridine (2.85 g, 17.17 mmol) in dichloromethane (15 cm^3) to a mixture of trifluoroacetic anhydride (7.5 cm^3, 11.15 g, 53.1 mmol), hydrogen peroxide (85%; 1.9 cm^3, 55.0 mmol) and dichloromethane which had just been heated under reflux for 30 minutes gave a dark-green mixture* containing tetrafluoro-4-nitrosopyridine. After a further period under reflux (1 hour), the mixture was poured onto ice and the organic layer [after being washed (1. saturated $NaHCO_3$ aq; 2. H_2O) and then dried ($MgSO_4$)] was evaporated to a low volume before being cooled (-78 °C) to cause the precipitation of a white solid. Recrystallization of this material from ethanol gave an analytically-pure sample of the white dimer (presumably) of 2,3,5,6-tetrafluoro-4-nitrosopyridine (1.12 g, 6.22 mmol, 36%), nc, [Found: C, 33.0; F, 42.4; N, 15.8%; *M* (mass spec.), 180. $C_5F_4N_2O$ requires C, 33.3; F, 42.2; N, 15.6%; *M*, 180], m.p. 63.5-65.0 °C (melts to a blue-green liq.),** with consistent spectroscopic properties.

[+] Obtainable commercially (Aldrich) or easily made from pentafluoropyridine (Aldrich) + NH_3 aq in EtOH [3a] or, preferably, THF [3b].

* Others [4] previously noted the rapid development of a green colour whilst carrying out this oxidation to procure tetrafluoro-4-nitropyridine.

** With respect to the dimer $\rightleftharpoons$ monomer equilibrium, therefore, tetrafluoro-4-nitrosopyridine is analogous to 4-bromo-2,3,5,6-tetrafluoronitrosobenzene but not pentafluoronitrosobenzene, which is monomeric in the crystalline (blue-green) as well as the liquid or dissolved state [5].

Like pentafluoronitrosobenzene [6], tetrafluoro-4-nitrosopyridine reacts with diazoalkanes to yield nitrones; e.g. with diphenyldiazomethane in light petroleum at ice temperature smooth evolution of nitrogen occurs to yield a product from which benzophenone and analytically-pure *C*,*C*-diphenyl-*N*-(tetrafluoro-4-pyridyl)nitrone (36% yield), its cyclic isomer 3,3-diphenyl-2-(tetrafluoro-4-pyridyl)oxaziridine (11%), and bis(tetrafluoro-4-pyridyl)diazene oxide (17%) have been isolated. This aspect of the chemistry of the nitrosopyridine, and its use as a source of tetrafluoro-4-pyridylnitrene, are under investigation.

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