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AROMATIC POLYFLUORO-COMPOUNDS—LII[1]

THE THERMAL DECOMPOSITION OF 1,2,3,4-TETRAFLUORO-5,8-DIHYDRO-5,8-(N-METHYLIMINO)-NAPHTHALENE

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Abstract—The thermal decomposition of 1,2,3,4-tetrafluoro-5,8-dihydro-5,8-(N-methylimino)-naphthalene has been studied in solvents, at 150–180° the sole isolable product being 1-methyl-2-(2′,3′,4′,5′-tetrafluorophenyl)-pyrrole. In the gas phase at 300–350° the products depended on the contact time and mode of addition to the pyrolysis tube. Thus, depending on the conditions the above mentioned. pyrrole, 1,2,3,4-tetrafluoronaphthalene, 2-(2′,3′,4′,5′-tetrafluorophenyl)pyridine, N-methyltetrafluorophthalimide and a compound believed to be 2-methyl-4,5,6,7-tetrafluoroisoindole-1,3-peroxide were obtained. Some reactions of these products are described.

PREVIOUSLY[2] we have reported the preparation of 1,2,3,4-tetrafluoro-5,8-dihydro-5,8-(N-methylimino)naphthalene (I) but only some of its simple reactions were described. We now wish to report some thermal decompositions of I.

Two methods of decomposition were used, heating in solvents and gas phase pyrolysis over glass beads.

When (I) was heated in ethylene glycol at reflux or in C_6H_6 at 160° (sealed tube), no gaseous products were detected and the product (II), a low melting solid, has spectral characteristics similar to those of 1-methyl-2-phenylpyrrole. Vigorous oxidation of II with $KMnO_4$ gave 2,3,4,5-tetrafluorobenzoic acid, suggesting that II contained a tetrafluorophenyl substituent. ^{19}F and ^1H NMR spectroscopy suggested II to be 2-tetrafluorophenyl-N-methylpyrrole. Further conformation of the gross structure was given by the mass spectrum which was in accord with this proposal.

Bromination of II in MeOH gave a crystalline solid (III) shown by mass spectrometry to contain two Br atoms. IR and NMR indicated further that III contained an N-Me, O-Me. C═O, C═C, and a tetrafluorophenyl group. These data taken together suggest III to be 1-methyl-2-methoxy-2-tetrafluorophenyl-2-(2′,3′,4′,5-tetrafluorophenyl)-3,4,-dibromopyrrolid-2-en-5-one. Although this result parallels the well known oxidation of pyrroles, by bromine water, to maleimides we find no report of methanolic bromine being employed. There is, however, a parallel in enamine chemistry, where methoxy-bromination is known[4] and probably follows an addition elimination sequence. Bromination of the pyrrole (II) with Br_2 in CCl_4 followed the expected pattern to yield 1-methyl-2-(2′,3′,4′,5-tetrafluorophenyl)-3,4,5-tribromopyrrole. It was found possible by a sequence of hydrogenation, LAH reduction and dehydrogenation to reconvert III→II albeit in small yield.

Gas phase pyrolysis of I in N_2 stream at 325° gave very volatile material, shown to be a mixture of C_2H_2 HCN, and a solid residue. Separation of the latter by column chromatography gave three fractions. The first was readily shown to be 1,2,3,4-

tetrafluoro-naphthalene.[5] The second was shown by IR spectroscopy to contain a carbonyl group at 1715 cm^{-1} (expected for a cyclic amide). The ^{19}F and ^{1}H NMR spectra showed an A_2X_2 system and an -NMe group respectively. Base hydrolysis of IV yielded tetrafluorophalic acid indicating it to be N-methyl-tetrafluorophthalimide. This was confirmed by synthesis from the phthalic acid and methylamine.

The third product, a crystalline solid (V), had ^{19}F and ^{1}H NMR spectra indicating a tetrafluorophenyl substituted aromatic, probably a pyridine. This was confirmed by the mass spectral cracking pattern, exact mass measurement and elemental analysis. The UV spectrum of V was similar to those of 2, and 3-phenylpyridines but very unlike that of 4-phenyl pyridine. ^{1}H NMR spectroscopy suggests that two protons at very low field are next to nitrogen *c.f.* 3-phenylpyridine. Thus, V is probably 3-(2′,3′,4′,5′ tetrafluorophenyl)pyridine. Treatment of V with dinitrochlorobenzene followed by aniline gave a red compound and the expected UV absorption at 350 nm characteristic of pyridines. Unfortunately a correct analysis could not be obtained for the anil which appeared to be contaminated with 2,4-dinitro-aniline.

Pyrolysis of I by addition to a preheated chamber at 170° (causing rapid evaporation into the pyrolysis tube at 325°) followed by working up without heating of the products gave a different result. None of the phthalimide was obtained, instead an ether insoluble solid VI which decomposed to the phthalimide IV when a slurry in ether, MeOH or cyclohexane was warmed to *ca.* 30°. Mass spectrometry of VI showed peaks at 219 and 203 which represent the loss of one and two oxygen atoms from a compound of empirical formula $C_9H_5F_4NO_2$. These results suggest VI could be 2-methyl-4,5,6,7-tetrafluoroisoindole-1,3-peroxide. Isoindole peroxides are well known in the literature usually being prepared by the reaction of oxygen with isoindoles.[6] They have also recently been postulated as being intermediates in the auto-oxidation of 2-butylisoindole to N-butyl phthalimide.[7] Their thermal decomposition does not, however, appear to have been studied.

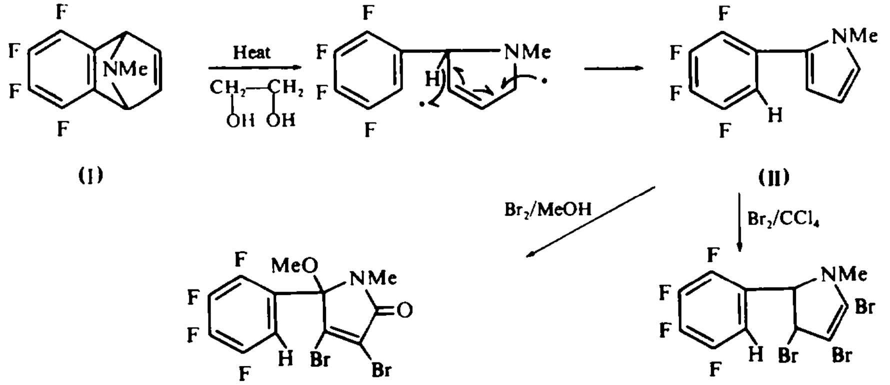
The ether soluble fraction from this experiment yielded the pyrrole II, the pyridine V and 1,2,3,4-tetrafluoronaphthalene. It seems likely that the pyrrole was produced in the preheated chamber rather than in the pyrolysis tube since we have shown subsequently that it passes through the tube at 325° unchanged, and it was not produced in the previous pyrolysis when no preheating was used.

When the pyrolysis was carried out at 325° in vacuo (0·7 mm) only the pyridine and the naphthalene were obtained.

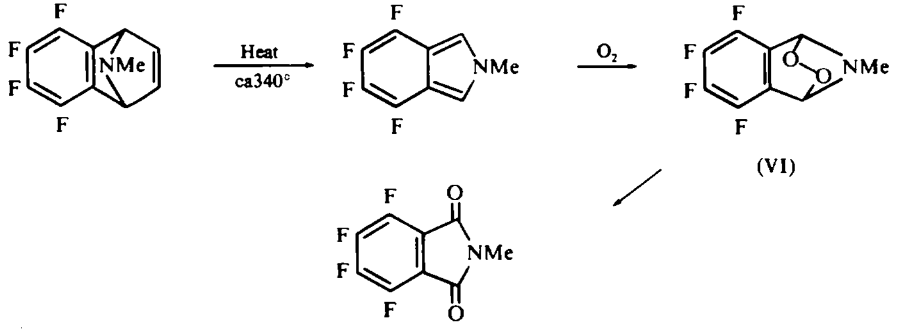
A number of attempts have been made, all of which were unsuccessful to synthesize both the pyrrole (II) and the pyridine (V) as added confirmation of their structure. For example reaction of N-methyl 2-pyrrolidone with tetrafluorophenyl lithium or tetrafluorophenyl magnesium bromide led only to products derived from the composition of these species to polyfluoro arynes which subsequently reacted in the expected manner.[2] Reaction of 3-bromo-pyridine with tetrafluorophenyl copper or in a crossed Ullmann reaction with bromo-2,3,4,5-tetrafluorobenzene gave only 2H,2′H-octafluorobiphenyl and no crossed product.

From the above results it would appear there are several different modes of decomposition for I. At low temps or in solvents a pathway as indicated in Scheme I seems reasonable to give only the pyrrole. Whilst at higher temps a number of competing pathways seem to be followed as outlined in Schemes II, III and IV. The presence of C_2H_2 in the volatile products suggests Scheme II as being likely. This is not without precedent in the fluorocarbon field.[8] The resulting isoindole might be expected to be readily oxidized to first the peroxide (VI) and then to the phthalimide (IV). The origin of the 1,2,3,4-tetrafluoronaphthalene is suggested by the HCN as shown in Scheme III. Loss of methylnitrene which subsequently gives HCN is a possibility.

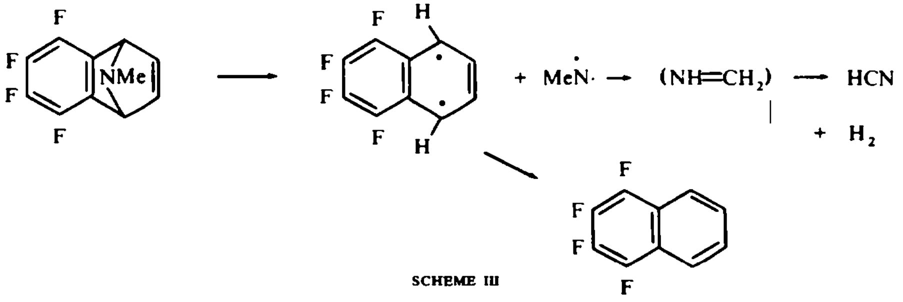
The origin of the pyridine is more difficult to explain. It might seem likely that it arises from rearrangement of the N-methyl pyrrole (II) but we have shown that under the reaction conditions this does not occur significantly. A possible sequence is set out in Scheme IV. The thermal cyclization is allowed by Woodward-Hoffman considerations and once the cyclic compound is formed the oxidation step does not seem unreasonable.



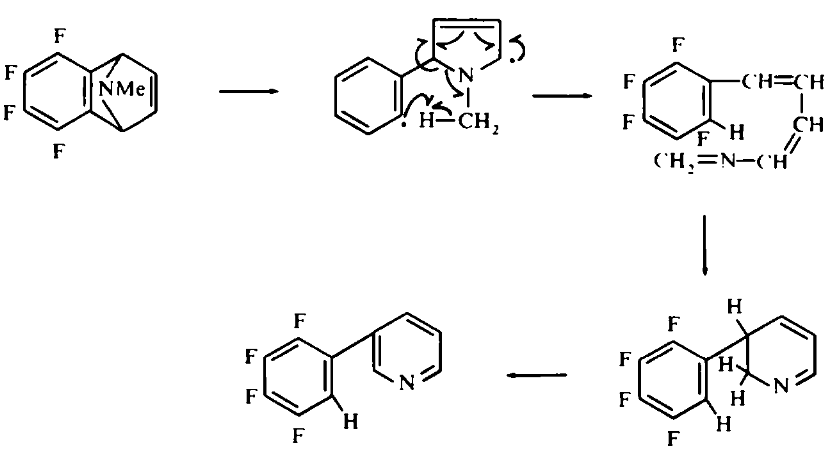
SCHEME I



(IV) SCHEME II



SCHEME III



(V)

SCHEME IV

EXPERIMENTAL

Thermal decomposition of 1,2,3,4-*tetrafluoro*-5,8-*dihydro*-5,8-(*N-methylimino*)-*naphthalene* (I). I (4·2 g) was heated in refluxing ethylene glycol (60 cm^3) for 4 hr. The deep red solution was extracted with ether (3 x 50 cm^3) and the extracts washed several times with water, dried ($MgSO_4$) and distilled to yield a red oil (3·4 g) which was distilled *in vacuo* from P_2O_5 to yield 1-*methyl* 2-(2',3',4',5'-*tetrafluorophenyl*)*pyrrole* (3·1 g, 74%) m.p. 28–29° (Found: C, 57·5; H, 3·3; M. 229. $C_{11}H_7F_4N$ requires C. 57·6; H, 3·1%; M. 229; λ_{max}EtOH 290,228 nm, ε 50,000, 31,000.

In a similar experiment but heating the imino compound (I) (0·8 g) in C_6H_6 (15 cm^3) at 180° in a sealed tube for 16 hr, the pyrrole (0·7 g) was obtained.

Heating I (0·51 g) in a sealed tube at 160° afforded the pyrrole (40%) with much tarry residue.

Oxidation of 1-*methyl*-2-(2',3',4',5 *tetrafluorophenyl*)*pyrrole*. The pyrrole (0·4 g) was heated to 100° in 4 N H_2SO_4 (5 cm^3) and KM_nO_4 (1·5 g) slowly added in small portions. The solution was heated and stirred for 1·5 hr, cooled and decolourized with sodium metabisulphite solution. The aqueous layer was further acidified and continuously extracted with ether for 15 hr. Working up yielded a small amount of brown oil which crystallized to a solid (0·09 g) with identical IR to that of 2,3,4,5-tetrafluorobenzoic acid.[9]

Bromination of 1-*methyl*-2-(2',3',4',5'-*tetrafluorophenyl*)-*pyrrole*. The pyrrole (0·33 g) in MeOH (30 cm^3) was stirred at 15° for 15 hr with bromine (0·5 cm^3). Ether (100 cm^3) was added and the solution washed several times with water and then sodium metabisulphite solution. The dried ($MgSO_4$) layer was distilled to yield on recrystallization from petroleum ether (b.p. 60–80°). 1-*methyl*-2-*methoxy*-2-(2',3',4',5-*tetrafluorophenyl*)-3,4-*dibromopyrrolid*-3-*en*-5-*one* (III) (0·5 g 80%) m.p. 115–117° (Found: C, 33·4; H, 1·8; M. 433, $C_{12}H_7Br_2F_4NO_2$ requires: C, 33·3; H, 1·6; M. 433) the mass spectrum showed 2 bromine atoms.

Bromine (1 cm^3) in CCl_4 (20 cm^3) was added dropwise to the pyrrole (0·8 g) in CCl_4 (20 cm^3). After initial decolourization, the solution turned deep purple and a black resinous precipitate formed. Evaporation of solvent afforded a purple gum (1·9 g). Purification (0·2 g) of this gum by column chromatography (silica gel C_6H_6) gave 1-*methyl*-2-(2',3',4',5'-*tetrafluorophenyl* 3,4,5,-*tribromopyrrole* (III) (0·15 g 87%) m.p. 111–114° (Found: C, 29·3; H, 1·3; N, 3·2; M. 466. $C_{11}H_4Br_3F_4N$ requires: C, 28·4; H, 0·9; N, 3·0%; M. 466) the mass spectrum showed 3 bromine atoms.

Reconversion of II *to* I. II (0·23 g) in EtOH (25 cm^3) was shaken with Pd/C (0·1 g) in H_2 atmosphere for 6 hr. Ether (50 cm^3) was added and the ether layer filtered and washed several times with water, dried ($MgSO_4$) and evaporated to an oil (0·16 g) (M. mass spec. 246) with no Br atoms. IR spectroscopy indicated a carbonyl group. Treatment of this oil in ether with LAH (0·08 g) at 15° for 1·5 hr and working up in the usual way afforded an oil (0·08 g), IR spectrum showed the absence of OH and carbonyl groups and the presence of a double bond. Heating this oil with Pd/C at 250° for 5 hr in a Carius tube yielded after distillation *in vacuo* a trace of an oil shown by IR to be 1-methyl-2-(2′,3′,4′,5-tetrafluorophenyl) pyrrole.

Pyrolysis of 1,2,3,4-*tetrafluoro*-5,8-*dihydro*-5,8-(*N*-*methylimino*) *naphthalene in the gas phase.* Resublimed (I) (2·65 g) was passed in three portions in a stream of O_2 free N_2 (5 l/hr through a pyrex tube (25 cm × 2·5 cm), packed with pyrex helices, heated to 325°. The eluted products were collected in a trap cooled in liquid air. On careful warming of the trap two gases were evolved the first was shown by IR spectroscopy to contain a strong bond at 729 cm^{-1} characteristic of C_2H_2. The second was trapped in 2N NaOH (10 cm^3) and treatment with $FeSO^4$ and H_2SO_4 gave a strong blue colour indicating the gas to be HCN.

The remaining pasty solid (1·74 g) was added to a dry column (50 cm × 4 cm) of silica gel and eluted with ether to yield in order of elution (i) 1,2,3,4-tetrafluoronaphthalene (0·59 g) 25·5% identical to an authentic sample;[5] (ii) N-methyl tetrafluorophthalimide (IV (0·29 g) 10·8% m.p. 156–158° (Found: C, 46·7; H, 1·6; N, 6·3; M. 233 0099 $C_9H_3F_4NO_2$ requires C, 46·5; H, 1·3; N, 6·0%; M. 233 0099) and identical to a sample prepared by heating tetrafluorophthalic anhydride with $MeNH_2$ followed by heating the half amide so formed with trifluoro-acetic anhydride and (iii) 3-(2′,3′,4′,5′-tetrafluorophenyl)pyridine (V) (0·35 g) 13·3% m.p. 91·5–93° (Found: C, 58·4; H, 2·5; M. 227·0358 $C_{11}H_5F_4N$ requires C, 58·2; H, 2·2%; M. 227·0358) λ_{max}EtOH 270,250 nm ε 2,900, 5000.

The pyrolysis was repeated but adding the adduct (I) (9·9 g) dropwise as a melt to a preheated (170°) evaporation chamber. The vapours were then passed as before through the pyrolysis tube. The pyrolysate was washed with cold ether to leave the relatively unstable 2-methyl-4,5,6,7-tetrafluoroisoindole-1,3-peroxide (VI) (2·77 g) 27·3%. The ether soluble extracts were washed with 4N-H_2SO_4 (2 × 50 cm^3) and evaporated to give a low melting solid (3·47 g) shown by IR spectroscopy to be 2-(2′,3′,4′,5′-tetrafluorophenyl) 1-methyl pyrrole (35%).

The acid wash was basified with 4 N NaOH, extracted with ether, dried ($MgSO_4$) and evaporated to give 3-(2′,3′,4′,5-tetrafluorophenyl)pyridine (0·62 g) 2·7%.

Repeat of the pyrolysis of I (7·3 g g) *in vacuo* at 0·7–0·8 mm pyrolysates (4·2 g) which afforded after work up as above no peroxide, the only isolated products being the pyridine (14%) unreacted starting material (65%) and 1,2,3,4-tetrafluoronaphthalene (21%).

Pyrolysis of 2-(2′,3′,4′,5′-*tetrafluorophenyl*)1-*methyl pyrrole.* The pyrrole (0·28 g) was pyrolyzed as above and starting material (0·24 g) recovered.

Thermal decomposition of 2-*methyl*-4,5,6,7-*tetrafluoroisoindoleperoxide.* The peroxide (1 g) was refluxed ether for 3 hr. The solvent was evaporated to yield a yellow solid (0·64 g). Chromatography on silica gel (C_6H_6 as eluant) gave (i) a colourless oil (0·11 g) which rapidly decomposed. Change of eluant to ether afforded N-methyl-tetrafluorophthalimide (0·25 g) identical with an authentic sample. Similar experiments with MeOH and cyclohexane gave the same result.

Hydrolysis of N-*methyl*-*tetrafluorophthalimide*:— The amide (0·093 g) was heated at 100° with 10% NaOH aq. (25 cm^3) for 5 hr. After acidification the mixture was continuously extracted with ether to yield tetrafluorophthalic acid (0·045 g) identical to an authentic sample.

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