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INTRAMOLECULAR NUCLEOPHILIC SUBSTITUTION OF FLUORINE IN α-PENTAFLUOROPHENYL-N-PHENYLNITRONE

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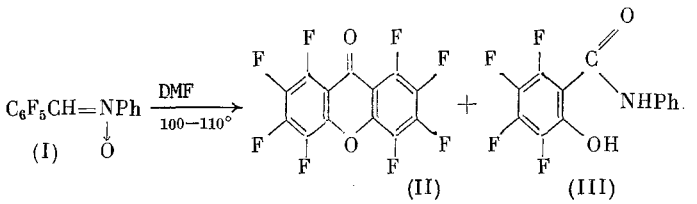
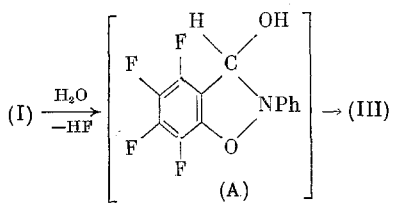
UDC 542.91:547.587.1'161:547.815.1'161

Intramolecular nucleophilic substitution reactions in polyfluoroaromatics most often involve N- or O- containing groups [1, 2] as the nucleophile, in particular the N-oxide function [3]. In this study we have used α-pentafluorophenyl-N-phenylnitrone (I) [4] as a representative polyfluoroaromatic nitrone.

The usual conditions for this reaction include heating in DMF, sometimes in the presence of base (KF, K_2CO_3, NaH) [1, 2]. We have shown that heating I in DMF leads to separation of a fluoride ion to give a mixture of octafluoroxanthone (II) [5] and tetrafluorosalicylanilide (III)



Formation of carboxanilides from aromatic nitrones in acid or basic media has been frequently reported [6, 7]. In the presence case it can be suggested that the intermediate 2,3-dihydro-1,2-benzisoxazole (A) is formed as a result of intramolecular attack of the O atom at a C atom of the pentafluorophenyl ring with decomposition under the reaction conditions by intramolecular elimination.



Novosibirsk Institute of Organic Chemistry, Siberian Branch of the Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 7, pp. 1579-1582, July, 1987. Original article submitted November 10, 1985.

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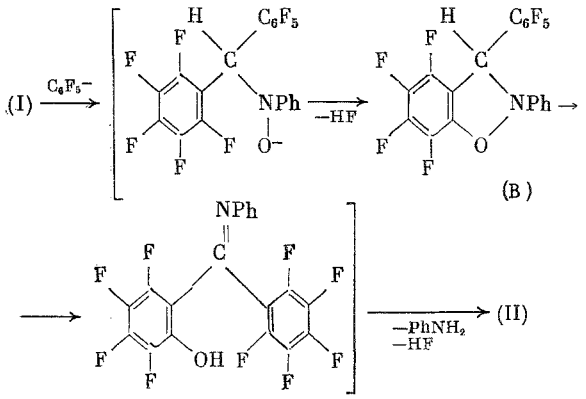
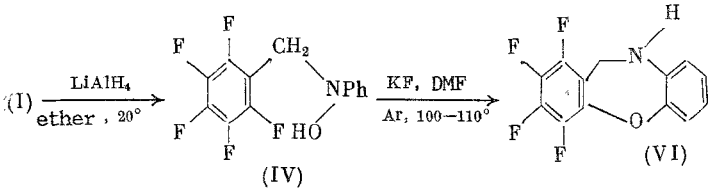
Anilide III did not form II on heating at 100-110°C in DMF and, thus, does not appear to be its precursor. It is possible that II may be formed according to the scheme*:



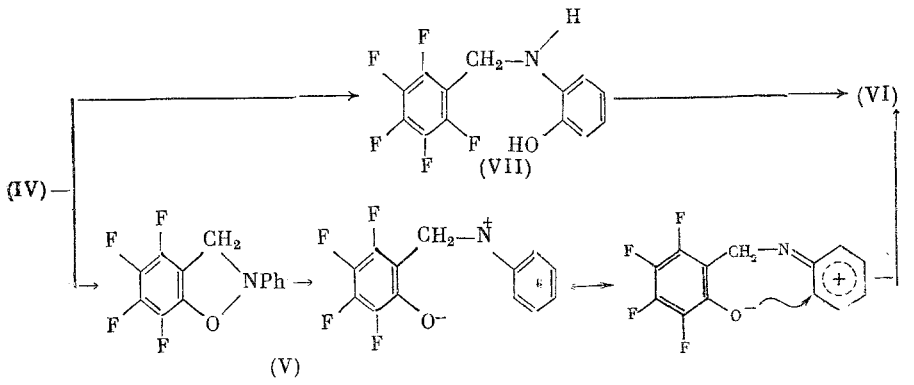
Appearance of the $C_6F_5^-$ anion was apparently due to partial haloform type decomposition of starting nitrone I. Evidently suppression of processes in which it participates can be made by lowering the medium basicity. In fact, upon heating I in DMF in the presence of a small amount of conc. HCl, the product (as judged by ^{19}F NMR) was only III with no contamination by II.

The schemes proposed above include the intermediate 2,3-dihydro-1,2-benzisoxazoles A and B. In order to assess their possible participation in the observed nitrone reactions we have obtained N-phenyl-N-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (IV) with the aim of cyclizing it to 2-phenyl-4,5,6,7-tetrafluoro-2,3-dihydro-1,2-benzisoxazole (V). The hydroxylamine IV was stable to heating at 100-110°C in DMF in an argon stream but formed 1,2,3,4-tetrafluoro-10,11-dihydro-dibenz[b,f]-1,4-oxazepine (VI) (previously reported by us [8]) in the presence of KF under the same conditions.



A mixture of VI and anilide III was obtained when the reaction was carried out in an oxygen atmosphere. The latter is apparently derived from nitrone I formed as a result of partial oxidation of the starting hydroxylamine IV. Heating at 60°C gave a mixture of I, IV, and VI.

Of the two possible pathways for formation of VI



the rearrangement of IV to o-hydroxy-N-(2,3,4,5,6-pentafluorobenzyl)aniline with subsequent cyclization is unlikely. In the first place, rearrangement of phenylhydroxylamines to aminophenols is an acid-catalyzed intermolecular process [9]. In the second, it is known that aminophenol (VII) is not changed upon heating with KF in DMF at 100°C. A more likely

*Aniline formation shown by GLC.

route involves formation of the intermediate dihydro-1,2-benzisoxazole (V). Ready conversion of the heterocycle to 1,2-benzisoxazoles with the formation of the phenoxy anion and examples of their recyclization are given in [10]. The different modes of stabilization of the intermediates A, B, and V may be due to their structural features.

EXPERIMENTAL

IR spectra were recorded on a UR-20 instrument and ^1H and ^{19}F NMR spectra on a Varian A 56/60 A (60 and 56.4 MHz) with ^{19}F chemical shifts referred to C_6F_6. Mass spectra were recorded on an MS-3301 for determination of molecular weight. DMF was dried over NaX and NaA molecular sieves.

Heating α-Pentafluorophenyl-N-phenylnitrone (I) in DMF. a) I (0.58 g) and conc. HCl (0.1 ml) were stirred in DMF (20 ml) in a bath (100-110°C) for 1 h. The mixture was poured into water, the precipitate filtered off, washed with hexane, the residue (0.32 g) dissolved in benzene, and passed through a silica gel column (L 100/160). III (0.19 g, 35%) with mp 154-155°C (from benzene) was obtained. IR Spectrum (CCl_4, ν, cm^{-1}): 1640 (C=O), 2600-3300 (OH), 3470 (NH). PMR Spectrum ($(CD_3)_2CO$, δ, ppm): 7.10-6.68, 8.14, and 9.34 (5:1:1). ^{19}F NMR spectrum (DMF, δ, ppm): −8.3, 1.41, 6.7, and 19.6 (1:1:1:1). Found: C 55.14; H 2.45; F 26.49; N 4.91%; mol. wt. 285. $C_{13}H_7F_4NO_2$. Calculated: C 54.74; H 2.48; F 26.65; wt. 285.

b) I (0.58 g) in DMF (20 ml) was stirred for 1 h at 100-110°C, the mixture poured into water and the precipitate filtered off to give 0.38-0.41 g of a mixture of II and III (content of II = 10-90% by ^{19}F NMR). Recrystallization from alcohol and identification by melting point and infrared spectral comparison with an authentic sample showed II to be octafluoroxanthone [5].

The filtrate was basified with aqueous ammonia, extracted with ether, and aniline identified in the ether solution by GLC.

N-Phenyl-N-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (IV). I (5.74 g) was added cautiously at 20°C to $LiAlH_4$ (0.76 g) in absolute ether (100 ml). The mixture was held for 1 h, poured into iced dilute HCl and extracted with ether. The ether layer was washed with aqueous $NaHCO_3$, water, dried with $MgSO_4$, evaporated and the residue washed with hexane to give IV (95%) with mp 149-151°C (from pet. ether-benzene). IR spectrum: 3000-3500 and 3580 (OH). PMR Spectrum (CD_3Cl, δ, ppm): 4.34 (CH_2), 6.50 (OH), and 7.30 (Ph). ^{19}F NMR spectrum (THF, δ, ppm): −1.1, 6.4, and 21.6 (2:1:2). Found: C 53.82; H 2.83; F 33.00; N 4.70 %; mol. wt. 289. $C_{13}H_8F_5NO$. Calculated: C 53.99; H 2.79; F 32.85; N 4.84%; mol. wt. 289.

Heating Hydroxylamine (IV) in DMF. a) IV (0.29 g) and anhydrous KF (0.29 g) in DMF (10 ml) were heated for 3 h at 100-110°C in a stream of argon. The mixture was poured into water and extracted with ether. The ether solution was washed with water, dried ($MgSO_4$), and evaporated to give the product (0.29 g). Chromatography on a silica gel column (L 100/160) in benzene, evaporation and washing the residue with hexane gave VI (0.15 g, 56%) with mp 66-68°C (cf. [8]).

b) IV (0.2 g) and anhydrous KF (0.2 g) in DMF (10 ml) were stirred for 5 h at 100-110°C and worked up as for a) to give a mixture (0.2 g) of III and VI (1:4 according to ^{19}F NMR).

c) IV (0.2 g) and anhydrous KF (0.2 g) in DMF (10 ml) were stirred for 9 h at 60°C. A typical product contained IV, I, and VI in the ratio of ∿5:2:3 (^{19}F NMR).

Heating o-Hydroxy-N-(2,3,4,5,6-pentafluorobenzyl)aniline (VII) in DMF. VII (0.2 g), obtained according to [8], and anhydrous KF (0.2 g) in DMF (10 ml) were stirred for 3 h at 100-110°C. The usual workup gave VII (0.2 g) unchanged (^{19}F NMR).

CONCLUSIONS

1. Heating α-pentafluorophenyl-N-phenylnitrone in DMF at 100-110°C gave a mixture of tetrafluorosalicylanilide and octafluoroxanthone.

2. Heating N-phenyl-N-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine in DMF with an hydrous KF in an argon atmosphere gave 1,2,3,4-tetrafluoro-10,11-dihydrodibenz[b,f]-1,4-oxazepine.

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INTRAMOLECULAR REARRANGEMENT WITH RING CONTRACTION OF 1,4-DIHYDROXY-3-BROMO-2,2,6,6-TETRAMETHYLPIPERIDINE

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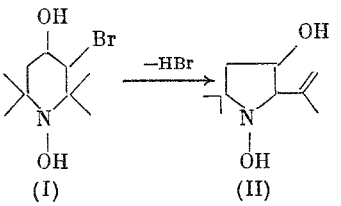
B. V. Rozynov, and S. R. Osmanova

UDC 542.952.1:547.823'141

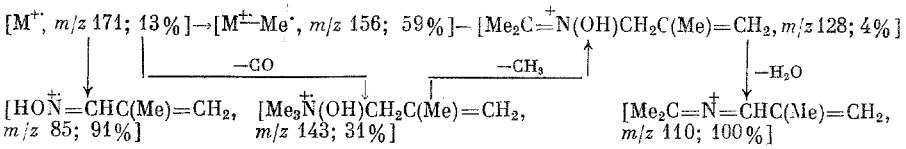
The synthesis and investigation of 3-halo derivatives of 2,2,6,6-tetramethylpiperidines is described in [1-3]. In this article it is shown that derivative (I) splits off HBr on exposure to bases and that as a result of intramolecular rearrangement with ring contraction it forms 1,3-dihydroxy-2-(2'-propenyl)-5,5-dimethylpyrrolidine (II) with a yield of 85-95%.



(1)

The reaction is carried out under the action of alcoholic alkali at about 20°C or by refluxing with amines in benzene or chloroform.

The structure of rearrangement product (II) was determined on the basis of chemical properties, but also of data from the IR, PMR, and mass spectra. In the mass spectrum of (II) an M^+ peak of m/z 171 is found, whose fragmentation is in agreement with the proposed structure:



On comparison of the IR spectra of compounds (I) and (II) (Table 1) it is clear that in (II) there are, in addition to the OH band, bands of the groups =C–H and C=C. Comparison of the PMR spectra of compounds (I) and (II) (Table 1) allows one to conclude that in (II), just as in (I), there is a CH_2 unit and a CHOH group, but from the two Me_2C groups of hydrobromide (I) there remains only one in (II) and the second has been transformed into an isopropenyl group. With an excess of MeCOCl compound (II) gives the O,O-diacetylated product (III). In the IR spectrum of (III) there is an ester carbonyl absorption at 1760 cm^{-1}, and in the PMR spectrum there are two singlets of MeCOO group at 1.87 and 1.90 ppm.

Institute of Chemical Physics, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 7, pp. 1582-1587, July, 1987. Original article submitted November 22, 1985.

0568-5230/87/3607-1461$12.50