Journal of Fluorine Chemistry, 28 (1985) 89–98

INTERACTION OF PENTAFLUOROPHENOL WITH LEAD TETRAACETATE IN ACIDS

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SUMMARY

The ability of polyfluorinated hydroxyaromatic compounds to be oxidised by radical and ionic mechanisms is discussed. Oxidation of pentafluorophenol by lead tetraacetate in hydrogen fluoride and trifluoroacetic acid gave the products of a reaction proceeding by an ionic mechanism - hexafluorocyclohexa-2,5-dienone and trifluoroacetoxydienones respectively.

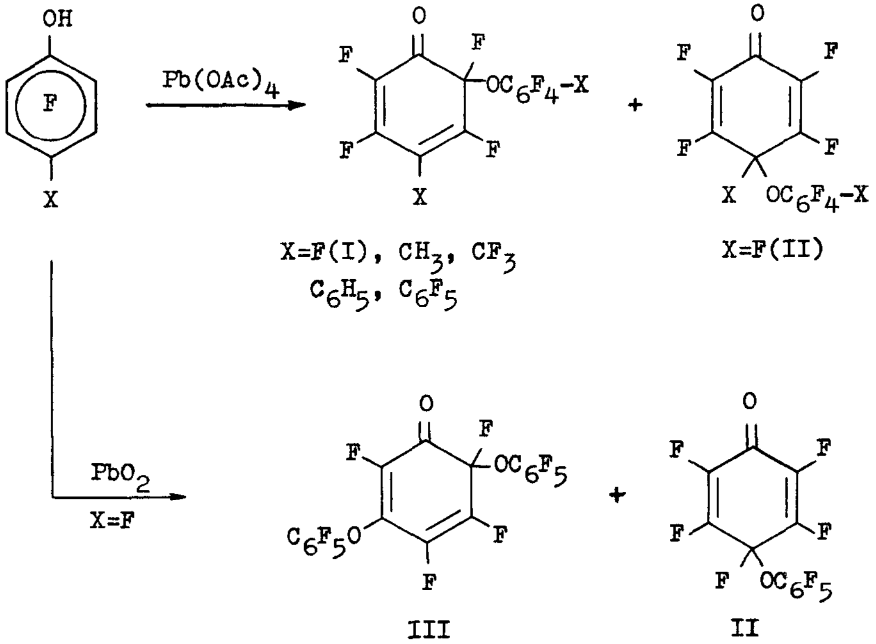
INTRODUCTION

Earlier we have shown that oxidation of pentafluorophenol [1] and 4-X-substituted tetrafluorophenols [2] by lead tetraacetate under mild conditions (room temperature, inert solvents) proceeds by a radical mechanism and leads to the formation of dimers of the phenoxyl radicals. The main route of dimerisation of polyfluorinated phenoxyl radicals is C_2-O dimerisation and in cases of 4-substituted phenols this is a single route. For the model of radical oxidation we used the reaction of pentafluorophenol with lead dioxide. The reaction gave dimer II and the product of further transformation of dimer I - compound III. It should be noted that earlier Denivelle[3] wrongly assigned to compound III the structure perfluoro-4-(4'-phenoxyphenoxy) cyclohexa-2,5-dienone.

Using the reactions of heptafluoronaphthols-1 and -2 with lead tetraacetate [4] as an example, we showed the possibility of making oxidations proceed by radical or ionic routes by

0022-1139/85/$3.30

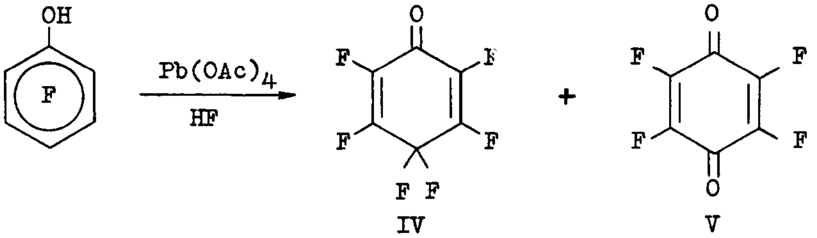
varying the reaction conditions. These routes lead to different products: radical oxidation gives dimers of naphthoxyl radicals, and ionic oxidation affords acetoxy derivatives of oxodihydronaphthalenes. We assumed that oxidation of heptafluoronaphthols proceeds via the intermediate formation of lead naphthoxytriacetate, which, depending on the reaction conditions, can undergo either homolytic or heterolytic decomposition, giving respectively naphthoxyl radicals or naphthoxylium cations. The radical route will take place if the reaction is conducted at low temperature and in inert non-polar solvents. In order to make the reaction proceed by the ionic route, it is necessary to conduct it in a polar solvent and at high temperature. Heterolysis is also promoted by boron trifluoride as a catalyst. This mechanism of oxidation of heptafluoronaphthols-1 and -2 by lead tetraacetate seems to be of a sufficiently general character to be used for interpreting the results of the reactions of any hydroxyaromatic compounds with lead tetraacetate.



RESULTS AND DISCUSSION

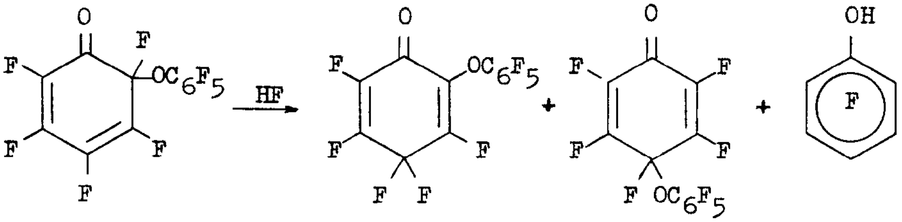
By contrast with heptafluoronaphthols-1 and -2, oxidation of pentafluorophenol by lead tetraacetate at a **high temperature** (100°C) in the presence of boron trifluoride, i.e. under the conditions of the ionic route, gave a mixture of the products of both ionic and radical routes, which we did not manage to separate. In order to make this reaction proceed by the ionic route, we used a modification of the oxidizer. It is known that in the presence of acids, lead tetraacetate undergoes anion exchange leading to the formation of another salt of tetravalent lead [5-8], for example, when the oxidation is conducted in HF [6] or trifluoroacetic acid [7], the oxidants are respectively lead tetrafluoride and lead tetra(trifluoroacetate). During oxidation of phenols under these conditions, proceeding by the ionic route, the dienone accepts the acid used instead of the acetoxy group [8].

The main product of the reaction of pentafluorophenol with lead tetraacetate in anhydrous hydrogen fluoride was hexafluorocyclohexa-2,5-dienone (IV), identified by comparison of its ^{19}F NMR spectrum with that of an authentic sample [9].



Fluoranil (V) formed in a small amount is, presumably, the product of hydrolysis of compound (IV). The absence of pentafluorophenoxyl radical dimers (I) and (II) among the products of this reaction may indicate that the reaction proceeds exclusively by the ionic route. The dimers (I) and (II) cannot be precursors of compounds (IV) and (V), since the para-quinoid dimer (II) has been reported to be stable to hydrogen fluoride [10], and the behaviour of ortho-quinoid dimer (I) in HF was studied by us.

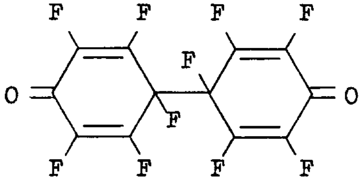
Interaction of compound (I) with hydrogen fluoride leads to perfluoro-2-phenoxycyclohexa-2,5-dienone (VI), identified by comparison of its ^{19}F NMR spectrum with that of an authentic sample [10], and to the product of partial isomerisation of compound (I), dimer (II).



I VI II

Apart from compounds (II) and (VI), the reaction mixture contained a small amount (≤10%) of pentafluorophenol. Pentafluorophenol is possibly formed by decomposition of compound (I) by HF. Such decomposition has been reported in the literature for the dimer of the 1-heptafluoronaphthoxyl radical [10]. The ratio between compounds (VI) and (II) is almost independent of the order of addition of the reagents and the reaction temperature. Isomerisation of compound (I) to give compounds (VI) and (II) seems to proceed by different mechanisms. The rearrangement of dimer (I) to compound (VI) is an HF-catalysed 1,3-allylic rearrangement [11]. We have also found boron trifluoride to have a similar catalytic effect [12]. Isomerisation of dimer (I) to dimer (II) proceeds, presumably, via migration of the pentafluorophenoxy group in the arenonium ion formed by protonation of compound (I) [13]. Earlier we have reported a thermal rearrangement of compound (I) to compound (II) proceeding via intermediate dissociation to pentafluorophenoxyl radicals [14], but it occurs at temperatures higher than 60°C. The acid-catalysed rearrangement of compound (I) to compound (II) has also been reported by us for solutions of compound (I) in acetic and trifluoroacetic acids [14].

It is interesting to compare our results on the oxidation of pentafluorophenol by lead tetraacetate in HF with the data on the electrolysis of pentafluorophenol in HF in the presence of potassium fluoride or antimony pentafluoride [15]. The authors of [15] showed the main reaction product to be hexafluorocyclohexa-2,5-dienone (IV), which is formed possibly by oxidation of pentafluorophenoxyl radicals to the corresponding cations and reaction of the latter with the medium. This route is confirmed by the formation of dimer (II). In addition to compounds (IV) and (II), the authors of [15] reported formation of a compound, which, on the basis of molecular weight determined by chromatomass-spectrometry, was wrongly (in our opinion) assigned the structure of the C-C dimer of the pentafluorophenoxyl radical (VII):

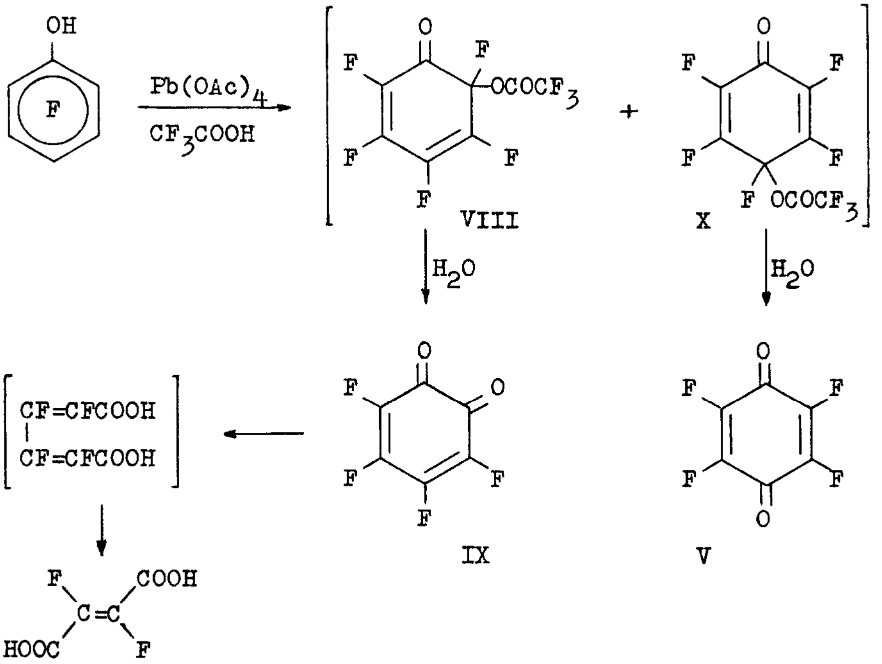


VII

This compound seems to be actually the product of isomerisation of the C_2-O dimer of pentafluorophenoxyl radical (I) by HF - compound (VI).

Oxidation of pentafluorophenol by lead tetraacetate in trifluoroacetic acid gave compounds extremely sensitive to moist air. A low-yield fraction obtained by distillation of the reaction mixture contains, according to ^{19}F NMR data, a mixture of products in which the main component has six signals in the ^{19}F NMR spectrum with the following chemical shifts (from C_6F_6 as an internal standard): -5.4 (F^2, ddt, J_{25} 21.0, J_{26} 10.0, $J_{24}=J_{23}$ 2.5 Hz); -12.3 (F^5, dd, J_{56} 30.0, J_{52} 21.0 Hz); -13.1 (F^4, dt, J_{46} 12.0, $J_{43}=J_{42}$ 2.5 Hz); -31.9 (F^3, dt, J_{36} 6.0, $J_{34}=J_{32}$ 2.5 Hz); -38.8 (F^6, dddd, J_{65} 30.0, J_{64} 12.0, J_{62} 10.0,

J_{63} 6.0 Hz); -87.5 (CF_3) ppm. The ratio of intensities was 1:1:1:1:1:3, respectively. The fine structure analysis and comparison with the ^{19}F NMR spectra of polyfluorinated cyclohexa-2,4-dienones [9] allowed us to assign to this compound the structure 6-trifluoroacetoxypentafluorocyclohexa-2,4-dienone (VIII). Hydrolysis of the mixture of products of the oxidation of pentafluorophenol by lead tetraacetate in trifluoroacetic acid gave a mixture of tetrafluoro-1,2-benzoquinone (IX) and fluoranil (V). This suggests that the precursors of quinones (IX) and (V) are respectively 6-trifluoroacetoxypentafluorocyclohexa-2,4-dienone (VIII) and 4-trifluoroacetoxypentafluorocyclohexa-2,5-dienone (X).



Apart from the signals of quinones (IX)and (V), the ^{19}F NMR spectrum of the hydrolysis products contains a singlet at -19.5 ppm from C_6F_6 (internal) ascribed by us to the fluorine atoms of difluorofumaric acid [16]. Difluorofumaric acid is, possibly, the product of further oxidation of quinone (IX) to tetrafluoromuconic acid, the transformation of which to give a mixture of difluorofumaric and difluoromaleic acids by treatment with acetic peracid has been reported [16].

The products of oxidation of pentafluorophenol by lead tetraacetate in trifluoroacetic acid also did not contain the dimers of pentafluorophenoxyl radical, which may indicate the ionic route of the reaction.

To sum up, the route of oxidation of polyfluorinated hydroxyaromatic compounds by lead tetraacetate may be chosen by varying the reaction conditions (temperature, solvent, oxidizer modification).

EXPERIMENTAL

Oxidation of pentafluorophenol by $Pb(OAc)_4$ in HF

Anhydrous HF (20 ml) and a solution of pentafluorophenol (8.0 g) in 20 ml of Freon 113 were placed in a polyethylene vessel. The vessel was cooled to 0°C, then 19 g of lead tetraacetate was added in small portions (much heat is evolved) over 1 h, with intermittent shaking of the vessel. The reaction mixture was kept for 30 min at 20°C, then poured onto ice. The organic layer was separated and the aqueous layer extracted with ether (3 x 50 ml). The extract was combined with the organic layer and washed with 8% aqueous $NaHCO_3$ till evolution of gas stopped. The organic layer was dried over anhydrous Na_2SO_4. The ether and Freon 113 were distilled off. The residue containing, as shown by ^{19}F NMR, ~72% of compound IV and ~5% of compound V, was distilled and a fraction boiling at 110-120°C collected to give 5.2 g of light yellow liquid, identified by comparison with the ^{19}F NMR spectrum of authentic hexafluorocyclohexa-2,5-dienone.

Interaction of perfluoro-6-phenoxycyclohexa-2,4-dienone with HF

a) Anhydrous HF (5 ml) was added to 1.0 g of compound I and the solution was stirred at 20°C for 2.5 h. Then it was poured into a mixture of ice and ether (20 ml of ether and 50 g of ice). The ether layer was separated and washed with water, then dried over anhydrous Na_2SO_4. The ether was distilled off. The residue was a light brown liquid containing, as shown by ^{19}F NMR, ~67% of perfluoro-2-phenoxycyclohexa-2,5-dienone (VI), ~14% of perfluoro-4-phenoxycyclohexa-2,5-dienone (II) and ~10% of pentafluorophenol.

b) Compound I (2.2 g) was added to 15 ml of anhydrous HF cooled to 0°C. The mixture was stirred at 0°C for 1 h and allowed to stand overnight for slow evaporation of HF at 20°C. The residue (2.1 g) containing, as shown by ^{19}F NMR, ~80% of compound VI, ~12% of compound II and ~5% of pentafluorophenol, was chromatographed on a column (125 x 1.5 cm) with SiO_2. The mixture was eluted with CCl_4 to yield 1.2 g of yellow oily product. The ^{19}F NMR spectrum of this compound is identical to that of authentic perfluoro-2-phenoxycyclohexa-2,5-dienone (VI). Further elution with carbon tetrachloride gave 0.3 g of compound II identified by the ^{19}F NMR spectrum.

Oxidation of pentafluorophenol by $Pb(OAc)_4$ in trifluoroacetic acid

a) A solution of 20.5 g of lead tetraacetate in 30 ml of trifluoroacetic acid was poured in small portions in to a solution of 8.3 g of pentafluorophenol in 20 ml of trifluoroacetic acid. After the addition was finished, the solution was kept for 10 min and 150 ml of water was poured into it. The precipitate was filtered off and washed with ether. The filtrate was extracted with ether. The ether solutions were combined and dried over anhydrous $CaCl_2$. The ether was distilled off in vacuum with the water bath temperature not higher than 40°C. To the residue, which was a solution of products in trifluoroacetic acid, benzene was added, and the azeotrope was distilled off in vacuum at a temperature not higher than 40°C. The procedure was repeated 4-5 times. The residue (7.5 g), a viscous orange mass, contained, as shown by ^{19}F NMR, ~39% of tetrafluoro-1,2-benzoquinone, ~17% of fluoranil and ~18% of difluorofumaric acid.

b) Lead tetraacetate (3.3 g) was dissolved at -10°c in 20 ml of trifluoroacetic acid and the mixture was stirred for 30 min. To the resulting solution, a mixture of 1.5 g of pentafluorophenol and 5 ml of trifluoroacetic anhydride was added. The solution was stirred for 1 h, then a mixture of acids and the reaction products was distilled off in 5 mmHg vacuum at room temperature. The mixture was then distilled at normal pressure, and three fractions were collected: fraction 1, b.p. up to 74°C - trifluoroacetic acid; fraction 2, b.p. 74-90°C - a mixture of acids and an unidentified product of yellow colour; fraction 3 (0.4 g), b.p. 90-105°C - a yellow liquid containing, as shown by ^{19}F NMR, trifluoroacetic acid, 6-trifluoroacetoxypentafluorocyclohexa-2,4-dienone (VIII) and unidentified products. The mixture could not be separated to components due to formation of an azeotrope with acetic and trifluoroacetic acids and high sensitivity of the products to moisture.

REFERENCES

1 L.S.Kobrina, V.N.Kovtonyuk and G.G.Yakobson, Zh. Org. Khim., 13 (1977) 1447.

2 V.N.Kovtonyuk, L.S.Kobrina and G.G.Yakobson, Izv. Sib. Otd. Akad. Nauk SSSR. Ser. Khim. Nauk (1984) (2) 119.

3 L.Denivelle and Huanh Anh-Hoa, Bull.Soc. Chim. Fr., (1974) 487.

4 V.N.Kovtonyuk, L.S.Kobrina and G.G.Yakobson, J. Fluor. Chem. 18 (1981) 587.

5 Y.Yukawa and M.Sakai, Bull. Chem. Soc. Jap., 36 (1963) 761.

6 D.D.Tanner and P. Van Bostelen, J. Am. Chem. Soc., 94 (1972) 3187.

7 R.O.C.Norman and M.Poustie, J. Chem. Soc.(C), (1969) 196.

8 P.Yates and H.Auksi, Can. J. Chem., 57 (1979) 2853.

9 N.E.Akhmetova, N.G.Kostina, V.I.Mamatyuk, A.A.Shtark and V.D.Shteingarts, Izv. Sib. Otd. Nauk SSSR. Ser. Khim. Nauk (1973) (6) 86.

10 A.G.Budnik, V.D.Shteingarts and G.G.Yakobson, Izv. Akad. Nauk SSSR. Ser. Khim., (1970) 1594.

11 A.S.Konde and P.MacGregor, Chem. and Ind., (1962) 460.

12 V.N.Kovtonyuk, L.S.Kobrina and G.G.Yakobson, Zh. Org. Khim., 15 (1979) 1447.

13 V.D.Shteingarts, Usp. Khim., 50 (1981) 1407.

14 L.S.Kobrina, V.N.Kovtonyuk and G.G.Yakobson, Izv. Sib. Otd. Akad. Nauk SSSR. Ser. Khim. Nauk (1978) (4) 132.

15 J.Devynck, A.Ben Hadid and H.Virelizier, J. Fluor. Chem., 14 (1979) 363.

16 L.S.Kobrina, N.V.Akulenko and G.G.Yakobson, Zh. Org. Khim., 8 (1972) 2165.