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OXIDATION OF PERFLUORONAPHTHOLS BY LEAD TETRAACETATE AND LEAD DIOXIDE

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SUMMARY

Depending on the reaction conditions, oxidation of perfluoronaphthols by $\text{Pb}(\text{OAc})_4$ proceeds by two routes. Under mild conditions (20°C) oxidation leads to the products of dimerisation of perfluoronaphthoxy radicals. At a higher temperature (80°C) the reaction leads to acetoxydienones. The mechanistic aspects of oxidation of perfluoronaphthols by $\text{Pb}(\text{OAc})_4$ are discussed.

INTRODUCTION

Previously we have reported that the oxidation of pentafluorophenol by $\text{Pb}(\text{OAc})_4$ leads exclusively to pentafluorophenoxy radical dimers: perfluoro-6-phenoxy-cyclohexa-2,4-dienone (I) and perfluoro-4-phenoxy-cyclohexa-2,5-dienone (II) in the ration 2:1 [1]. Formation of acetoxydienones, which are the typical products of oxidation of non-fluorinated phenols by $\text{Pb}(\text{OAc})_4$, has not been observed. The reaction has been found to proceed under kinetic control conditions, because dimer I isomerises to dimer II when heated [1,2].

RESULTS AND DISCUSSION

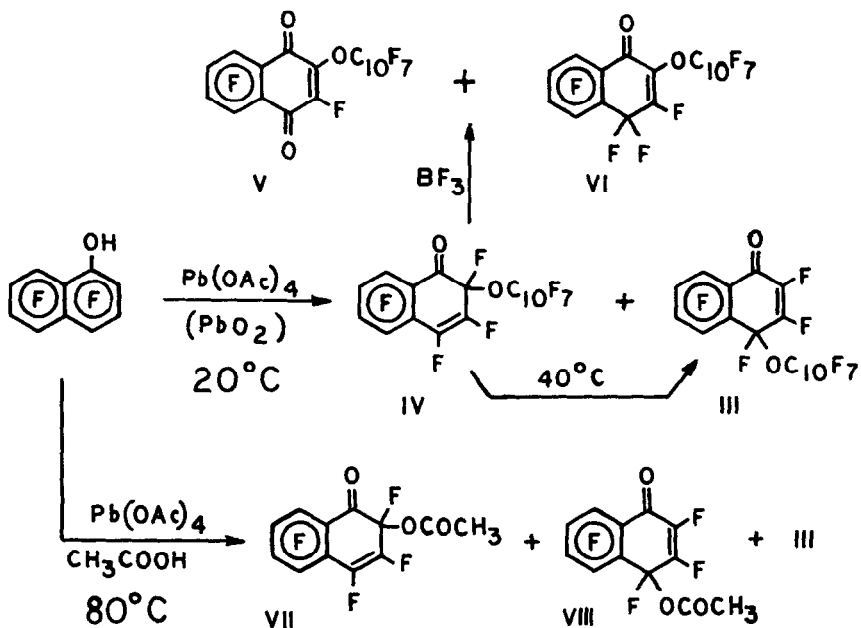
In this paper we report the results of oxidation of perfluoronaphthols-1 and -2 by $\text{Pb}(\text{OAc})_4$ and PbO_2 under various conditions.

Oxidation of perfluoronaphthol-1 at 20°C by $\text{Pb}(\text{OAc})_4$ in carbon tetrachloride or acetic acid and by PbO_2 in benzene leads to a reaction mixture

containing, according to ^{19}F NMR data, two compounds (III and IV) in approximately 1:1 ratio. The spectral data for compound III and the literature data on oxidation of perfluoronaphthol-1 by PbO_2 [3] led us to assign to this product the known structure of perfluoro-[1-oxo-4-(1'-naphthoxy)-1,4-dihydronaphthalene]. Compound IV, isolated in admixture with III, has the same molecular weight as the latter. This compound can be isomerized to compound III by heating it to 40°C or allowing it to stand at 20°C for one week. It is rather difficult to interpret the ^{19}F NMR spectrum of this compound because of overlapping signals and the presence of signals caused by compound III. We supposed that compound IV was perfluoro-1-oxo-2-(1'-naphthoxy)-1,2-dihydronaphthalene, and to confirm this structure used the ability of cyclohexa-2,4-dienones with a geminal CFX group to rearrange on treatment with BF_3 [4].

Treatment of a ca. 15:85 mixture of compounds III and IV with BF_3 in nitromethane solution leads to a mixture from which two compounds, (V and VI), have been isolated. Compound V was identified as perfluoro-2-(1-naphthoxy)-1,4-naphthoquinone because of the identity its ^{19}F NMR spectrum with that previously described [5]. The formation of this compound presumably occurs by the action of moisture in the air. According to the elemental analysis, compound VI has the same composition as compound III and IV. The spectral data led us to assign for the compound VI the structure of perfluoro-1-oxo-2-(1'-naphthoxy)-1,4-dihydronaphthalene. The structures of compounds V and VI unambiguously indicate that compound IV is perfluoro-1-oxo-2-(1'-naphthoxy)-1,2-dihydronaphthalene.

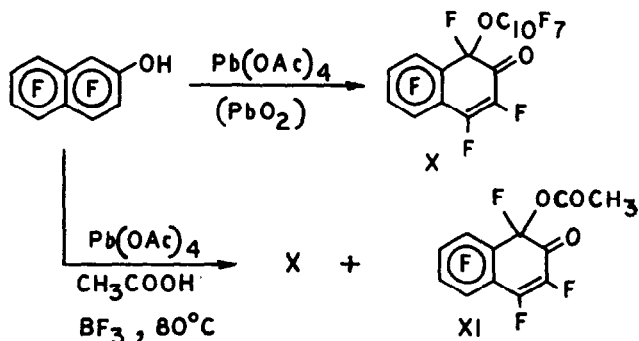
Oxidation of perfluoronaphthol-1 by $\text{Pb}(\text{OAc})_4$ in acetic acid at 80°C leads to a mixture from which dimer III and two other compounds have been isolated. According to their spectral data these compounds are 1-oxo-2-acetoxy-2,3,4,5,6,6,8-heptafluoro-1,2-dihydronaphthalene (VII) and 1-oxo-4-acetoxy-2,3,4,5,6,7,8-heptafluoro-1,4-dihydronaphthalene (VIII). By ^{19}F NMR the ratio of compounds VII and VIII in the reaction mixture is shown to be equal to 1.2:1. From the reaction mixture was also isolated 2-hydroxy-3,5,6,7,8-pentafluoro-1,4-naphthoquinone (IX), identified by its ^{19}F NMR spectrum [6]. Compound IX is not a primary product and its yield has been shown to depend on the reaction time and work-up procedure. The fact that compound VII is the precursor of compound IX follows from an experiment in which VII was heated with $\text{Pb}(\text{OAc})_2$ at 80°C for 30 min, and found to be converted completely to compound IX. Compound VIII remains unchanged under the same conditions during 2 hours. Compound VII undergoes no change at 80°C in the absence of $\text{Pb}(\text{OAc})_2$.



The oxidation of phenols by Pb(OAc)_4 to yield acetoxydienones is known to be catalyzed by BF_3 [7]. We have also investigated the oxidation of perfluoro-naphthol-1 by Pb(OAc)_4 at 20°C in the presence of BF_3 . The ^{19}F NMR spectrum of the reaction mixture shows compounds VII (~70%) and VIII (~30%) to be the main products.

Oxidation of perfluoronaphthol-2 by Pb(OAc)_4 , independent of the temperature (20°C , 80°C) and the solvent used, leads to perfluoro-2-oxo-1-(2'-naphthoxy)-1,2-dihydronaphthalene (X) as the main product. The same compound is also the main product of oxidation of perfluoronaphthol-2 by PbO_2 in benzene. But in the latter case, its yield depends on the extent of dilution, the ration of the reagents and the order of their addition, and varies from ~60% to quantitative.

BF_3 -catalyzed oxidation of perfluoronaphthol-2 by Pb(OAc)_4 leads to acetoxydienone formation as in the case of oxidation of perfluoronaphthol-1. However, we were able to obtain 2-oxo-1-acetoxy-1,3,4,5,6,7,8-heptafluoro-1,2-dihydronaphthalene (XI) in satisfactory yield only at 80°C (~40% of compound X and ~60% of compound XI).



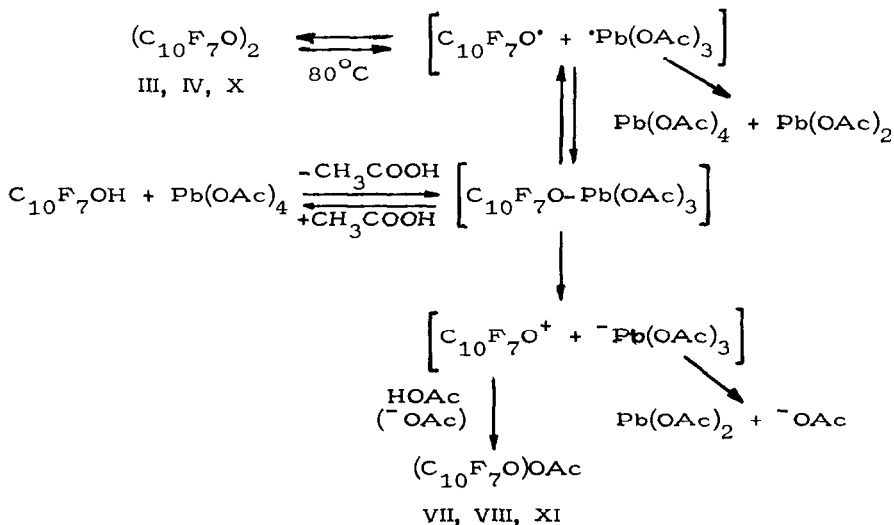
Thus the products of oxidation of perfluoronaphthols by Pb(OAc)_4 depend on the reaction conditions; under 'mild' conditions, the reaction leads to dimers products (III, IV and X), whereas oxidation at high temperature (80°C) and in the presence of BF_3 gives acetoxydienones (VII, VIII and XI).

Compounds III, IV and X are the typical products of dimerization of perfluoronaphthoxy radicals and their formation suggests the operation of a radical oxidation mechanism of perfluoronaphthols by Pb(OAc)_4 at 20°C . The complete identity of the products and their ratios in the reaction with PbO_2 , widely used to generate phenoxy radicals, offers indirect evidence for such a conclusion. The oxidation of perfluoronaphthol-1 by both reagents should be noted to proceed like oxidation of pentafluorophenol [1] under conditions of kinetic control, because of easy isomerization of dimer IV (on heating at 40°C) to dimer III, probably via intermediate dissociation into perfluoro-1-naphthoxy radicals. Such isomerization provides a reason why the dimer IV was not identified earlier in oxidation of perfluoronaphthol-1 by PbO_2 [3].

Acetoxydienones VII, VIII and XI formed in oxidation of perfluoronaphthols by Pb(OAc)_4 under more stringent conditions are probably the primary reaction products, rather than the products of further reactions of dimers III, IV and X, or of the corresponding perfluoronaphthoxy radicals produced by dissociation of X. This has been confirmed by the fact that in oxidation of perfluoronaphthol-1 by Pb(OAc)_4 at 20°C in the presence of BF_3 the formation of dimers III and IV has not been observed, whereas in the absence of BF_3 these dimers are the main reaction products. At the same time we have shown that heating of dimer III with Pb(OAc)_4 at 80°C fails to produce acetoxydienones VII and VIII and the dimer III is returned unchanged, though oxidation of perfluoronaphthol-1 under the same conditions leads to acetoxydienones VII and VIII. It has also been shown [8], that the independently generated 2,4,6-tris-tert-butylphenoxy radical is

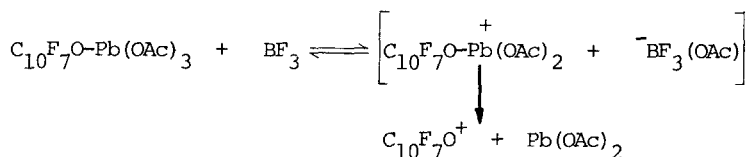
not oxidized by $\text{Pb}(\text{OAc})_4$ and does not yield the corresponding acetoxydienones. At the same time it has been shown that $\text{Pb}(\text{OAc})_4$ is a source of acetoxy radical even at 20°C [9] and the formation of acetoxydienones by a radical mechanism could be expected. Moreover, acetoxydienones have been shown to be the main products of electrochemical oxidation of phenols to the corresponding cations in acetic acid [10]. From these data, one may suggest that perfluoronaphthoxylium cations or the polarized structures of their precursors are responsible for the formation of acetoxydienones VII, VIII and XI rather than perfluoronaphthoxy radicals. The ratio of acetoxydienones VII and VIII (2.3:1) in oxidation of perfluoronaphthol-1 by $\text{Pb}(\text{OAc})_4$ in the presence of BF_3 may be indirect evidence for a non-radical reaction, since in the case of a radical mechanism that ratio must be approximately 1:1, as in the case of formation of the dimers III and IV in the absence of BF_3 . The ratio of acetoxydienones VII and VIII (1.2:1) obtained in the oxidation of perfluoronaphthol-1 by $\text{Pb}(\text{OAc})_4$ at 80°C is not a primary one, because of further transformation of compound VII to compound IX in that case. Taking that fact into account the primary ratio of acetoxydienones VII and VIII in that reaction would be 2-3:1.

Summarizing, the following mechanism of oxidation of perfluoronaphthols by $\text{Pb}(\text{OAc})_4$ is suggested: lead perfluoronaphthoxytriacetate, generated in the first stage of the reaction, undergoes either homolysis or heterolysis, depending on the conditions.



At 20°C, and in the absence of BF₃, the homolytic decomposition of the organo-lead intermediate to form perfluoronaphthoxy radicals and Pb(OAc)₃ will, presumably, be the only route of reaction. Dimerization of perfluoronaphthoxy radicals leading to dimers III, IV and X is irreversible at 20°C because the dimers are stable under these reaction conditions. At a higher temperature (80 - 100°C), perfluoronaphthoxy radical dimers can exist in equilibrium of homolytic decomposition towards the initial lead perfluoronaphthoxytriacetate and subsequent heterolysis of the latter. Really, oxidation of perfluoronaphthol-1 at 80°C has been reversed, the acetoxydienones VII and VIII being the main products. Lead perfluoro-1-naphthoxytriacetate, formed as an intermediate, probably, undergoes heterolysis at 80°C before, or concerted with an attack of nucleophile (acetic acid or acetate anion). Homolysis of lead perfluoro-1-naphthoxytriacetate with formation of dimer III under these conditions takes place insignificantly, or is reversible because of dissociation of dimer III at 80°C. In oxidation of perfluoronaphthol-2 by Pb(OAc)₄ under the same conditions the reverse of the reaction route has not been observed, dimer X being the main product as at 20°C. Only traces of the corresponding acetoxydienone XI has been detected (TLC) under these conditions.

The reversal of oxidation of perfluoronaphthols by Pb(OAc)₄ in the presence of BF₃ can be explained either by the increase in oxidation potential of Pb(IV) [11], or by initiation of the decomposition of lead perfluoronaphthoxytriacetate, as follows :



A similar route was suggested earlier to explain the catalytic effect of BF₃ during oxidation of methoxybenzenes by Pb(OAc)₄ [12].

The scheme of oxidation of perfluoronaphthols by Pb(OAc)₄ proposed in the present work involves two different reaction routes: radical and ionic, depending on the reaction conditions, modification of which allows the reaction to be completely shifted towards one of these routes. We consider these routes to be general enough to be used when discussing oxidation schemes for various phenols. The general trend in previous studies on oxidation of phenols by Pb(OAc)₄ was to explain reaction schemes on the basis of one of these routes (either the radical [13,14] or the ionic one [7,8,15]). That approach inevitably

resulted in contradictions between the adherents of the radical and the ionic mechanism, and, in fact, to the absence of clearness in the reaction mechanism despite a lot of experimental data. Study of the oxidation of perfluoronaphthols by $\text{Pb}(\text{OAc})_4$ has allowed us to separate both possible routes.

EXPERIMENTAL

IR spectra were recorded on a 'UR-20' spectrophotometer (solutions in CCl_4 or KBr tablets; NaCl prism), UV spectra on a 'SPECORD UV VIS' spectrophotometer (heptane solutions), ^{19}F NMR spectra on a 'VARIAN A56/60A' spectrometer (56.4 MHz), and ^1H NMR spectra - on a 'TESLA BS467' spectrometer (60 MHz).

Oxidation of perfluoronaphthol-1 by PbO_2

Perfluoronaphthol-1 (3.0 g) was added in small portions to a stirred suspension of PbO_2 (5.3 g) and anhydrous Na_2SO_4 (5.3 g) in dry benzene (100 ml) at 20°C . The mixture was stirred for 2 h. The solution was decanted and the precipitate was twice washed by decantation with benzene (20 ml). The benzene solution was filtered and evaporated in vacuum (20 mm Hg) at 20°C . The residue (3.5 g), a yellow orange solid, was chromatographed on a column (220 x 2.2 cm) with SiO_2 . Elution with CCl_4 at pressure of 0.3 at. led to 3 fractions. Fraction 1 (0.85 g): pale yellow crystals containing, by ^{19}F NMR, ~85% of perfluoro-1-oxo-2-(1-naphthoxy)-1,2-dihydronaphthalene (IV) and ~15% of perfluoro-1-oxo-4-(1'-naphthoxy)-1,4-dihydronaphthalene (III). Found: Mol.wt. 535, 536. $\text{C}_{20}\text{F}_{14}\text{O}_2$ requires: Mol.Wt. 538. Fraction 2 (0.95 g): pale yellow crystals containing, by ^{19}F NMR, ~60% of compound IV and ~40% of compound III. Fraction 3 (1.0 g): pale orange crystals, identified as perfluoro-1-oxo-4-(1'-paphthoxy)-1,4-dihydronaphthalene (III) (see [3]).

Interaction of perfluoro-1-oxo-2-(1'naphthoxy)-1,2-dihydronaphthalene (IV) with BF_3

A mixture of compounds III and IV (0.85 g) (see the previous experiment, fraction 1) was dissolved in nitromethane (40 ml) saturated with BF_3 . The solution was kept at 20°C for 3 h and then NaF (10 g) was added with stirring. The reaction mixture was left over-night, filtered and washed with ether (10 ml).

The filtrate was evaporated under vacuum (20 mmHg). The residue (0.7 g), yellow-orange crystals, was chromatographed on a column (10 x 3 cm) packed with SiO₂. Elution with CCl₄ yielded 0.5 g perfluoro-1-oxo-2-(1'-naphthoxy)-1,4-dihydronaphthalene (VI) (nc); m.p. 93 - 95°C. UV spectrum, λ_{\max} , nm (lg ϵ): 217 (4.83), 285 (4.03). IR spectrum, cm⁻¹: 1715m, 1710m (C = O, -FC = CF -); 1530s, 1500s, 1480s (fluorinated aromatic ring), ¹⁹F NMR spectrum (25% solution in CCl₄), ppm from C₆F₆ (internal)*: -6.9 (F³); -8.1 (F^{6'}, F^{7'}); -13.8 (F^{2'}); -15.5 (F⁷); -17.5, -19.4 (F^{5'}, F^{4'}, AB system, J_{peri}^{FF} 63 Hz); -18.2 (F⁶); -19.8 (F^{8'}); -25.6 (F³); -26.1 (F⁵, F⁸); -62.0 (F⁴). The ratio of intensities was 1:2:1:1:1:1:1:1:2:2, respectively. Found (%): C 44.96; F 49.72, 49.33; Mol.wt. 541, 543. C₂₀F₁₄O₂ requires (%): C 44.61; F 49.44; Mol.wt. 538. Further elution with ether yielded perfluoro-2-(1'-naphthoxy)-1,4-naphthoquinone (V), identified by ¹⁹F NMR spectroscopy.

Isomerization of perfluoro-1-oxo-2-(1'-naphthoxy)-1,2-dihydronaphthalene (IV)

Compound IV (0.1 g) and CCl₄ (0.4 g) were stored in an NMR spectral tube at 20°C for a week. ¹⁹F NMR analysis showed that compound IV had completely isomerized to compound III during that period.

At 40°C, compound IV was completely isomerized to compound III in ~10 hours.

Oxidation of perfluoronaphthol-1 by Pb(OAc)₄ at 20°C in CCl₄

A solution of perfluoronaphthol-1 (1.0 g) in CCl₄ (10 ml) was added dropwise to a suspension of Pb(OAc)₄ (1.5 g) in CCl₄ (20 ml). The reaction mixture was stirred for 1.5 h and the precipitate was removed by filtration. The filtrate was evaporated under vacuum (20 mmHg) at 20°C. According to ¹⁹F NMR data, the reaction mixture contained compounds III and IV in the ratio of ~1:1 and was identical with the reaction mixture formed by oxidation of perfluoronaphthol-1 by PbO₂.

* Assignments are hypothetical and made by comparison with fluorine chemical shifts in the spectra of 1-X-substituted heptafluoronaphthalenes [16], compound V [5] and polyfluorinated cyclohexadienones [17].

Oxidation of perfluoronaphthol-1 by $\text{Pb}(\text{OAc})_4$ at 80°C in acetic acid

$\text{Pb}(\text{OAc})_4$ (11.7 g) was added during 15 min. to a vigorously stirred solution of perfluoronaphthol-1 (7.0 g) in acetic acid (150 ml) at 80°C . After the addition was finished, the reaction mixture was cooled to 30°C , filtered and the precipitate washed with 50 ml of acetic acid. The filtrate was evaporated under vacuum (20 mmHg). Carbon tetrachloride (50 ml) was added to the residue and an azeotrope of acetic acid and CCl_4 was distilled off under vacuum. The procedure was repeated several times until the odour of acetic acid vanished. The residue, after distillation, was treated twice with 50 ml of benzene and several times with 50 ml of boiling benzene till the resinous elad-containing residue solidified. The benzene solution was filtered. The lead salts were combined and treated with 10% HCl (100 ml). The hydrochloric acid solution was extracted with ether (3 times with 100 ml). The extract was dried over CaCl_2 and the ether was distilled off under vacuum. The residue (2.7 g) was a pale yellow crystalline substance; m.p. (from benzene) $225\text{--}230^\circ\text{C}$ (in a sealed capillary tube); ^{19}F NMR spectrum (30% solution in CH_3CN), ppm from C_6F_6 (internal): -16.6 (F^3 , dd, J 4.0, $J \approx 1.5$ Hz); -16.8 (F^6 or 7 , td, J 18.5, $J \approx 10.3$ Hz); -18.8 (F^7 or 6 , tdd, J 18.5, $J \approx 11.5$, J 4.0 Hz); -24.8 (F^5 or 8 , dtd, J 18.5, $J \approx 10.3$, $J \approx 1.5$ Hz); -25.8 (F^8 or 5 , dt, J 18.5, $J \approx 11.5$ Hz). The ratio of intensities was 1:1:1:1:1, respectively. The ^{19}F NMR spectrum was identical with the spectrum of a sample of the known 2-hydroxy-3,4,5,6,7,8-pentafluoro-1,4-naphthoquinone (IX), obtained according to [6]. The benzene solution, after removal of lead salts, was evaporated under vacuum to give red viscous liquid, containing, according to ^{19}F NMR, $\sim 40.6\%$ of 1-oxo-2-acetoxy-2,3,4,5,6,7,8-heptafluoro-1,2-dihydronaphthalene (VII) and $\sim 34.4\%$ of 1-oxo-4-acetoxy-2,3,4,5,6,7,8-heptafluoro-1,4-dihydronaphthalene (VIII). The liquid was purified by column (220 x 2.2 cm) chromatography with SiO_2 . On elution of the mixture with $\text{CCl}_4/\text{C}_6\text{H}_6$ in the ratio of 10:1 by volume, 3 fractions were isolated. Fraction 1 (0.2 g) contained, by ^{19}F NMR, $\sim 65\%$ of dimer III and $\sim 20\%$ of compound VII. Fraction 2 (3.0 g), a red viscous liquid, contained according to ^{19}F NMR, $\sim 19\%$ of dimer III and $\sim 70\%$ of compound VII. This liquid (2.7 g) was distilled under vacuum (0.1 mmHg), the fraction collected at $70\text{--}90^\circ\text{C}$ was 1-oxo-2-acetoxy-2,3,4,5,6,7,8-heptafluoro-1,2-dihydronaphthalene (VII) (nc) (1.6g), a pale yellow liquid which crystallized on storage at 0°C . M.p. $49\text{--}52^\circ\text{C}$. UV spectrum, λ_{max} , nm (lg ϵ): 229 (4.48), 286 (3.48), 297 (3.44), 339 (3.45). IR spectrum,

cm^{-1} : 1760s, 1740s, 1730s (C=O, -FC=CF-); 1630m, 1520s, 1490s (fluorinated aromatic ring). ^1H NMR spectrum (20% solution in CCl_4 ; TMS (internal)); 2.12 (singlet) ppm. ^{19}F NMR spectrum (20% solution in CCl_4 ; ppm from C_6F_6 (internal)): -10.5 (F^3 , dm, J_{32} 27 Hz); -11.6 (F^7 , m); -20.0 (F^6 , m); -19.6. -22.9 (F^4 , F^5 , AB system, J_{45} 74, J_{56} \approx 18 Hz); -29.1 (F^8 , m); -36.0 (F^2 , dd, J_{23} 27.0, J_{11} Hz). The ratio of intensities was 1:1:1:1:1:1:1, respectively. Found (%): C 43.83, 43.60; H 0.92, 0.97; F 40.99, 40.94; Mol.wt. 326, 329. $\text{C}_{12}\text{F}_7\text{H}_3\text{O}_3$ requires (%): C 43.90; H 0.91; F 40.55; Mol.wt. 328. Fraction 3 (1.7 g), light yellow crystals, was 1-oxo-4-acetoxy-2,3,4,5,6,7,8-heptafluoro-1,4-dihydronaphthalene (VIII) (nc). M.p. 79-81°C. UV spectrum, λ_{max} , nm (lg ϵ): 240 (3.98), 279 (3.58), 297 shoulder (3.52). IR spectrum, cm^{-1} : 1790s, 1770s, 1730s, 1710s (C=O, -FC=CF-); 1635m, 1530s, 1500s (fluorinated aromatic ring). ^1H NMR spectrum (30% solution in CCl_4 ; δ from TMS (internal)): 2.12 (singlet) ppm. ^{19}F NMR spectrum (30% solution in CCl_4 ; ppm from C_6F_6 (internal)*): -12.9 (F^2 , td, J_{23} \approx J_{24} 8.5, J_{27} \approx 2.0 Hz); -14.1 (F^7 , tdt, J_{76} \approx J_{78} 19.5, J_{75} 7.0, J_{72} \approx J_{74} \approx 2.5 Hz); -18.1 (F^6 , tdd, J_{67} \approx J_{65} 19.5, J_{68} 12.0, J_{63} 4.5 Hz); -19.8 (F^3 , ddd, J_{34} 27.5, J_{32} 8.5, J_{36} 4.5 Hz); -24.1 (F^5 , m); -25.8 (F^8 , dt, J_{87} 19.5, J_{86} \approx J_{85} 12.0 Hz); -47.9 (F^4 , dtd, J_{43} 27.5, J_{45} \approx J_{42} 8.5, J_{47} \approx 2.5 Hz). The ratio of intensities was 1:1:1:1:1:1:1, respectively. Found (%): C 43.62, 43.83; H 1.14, 1.16; F 41.07, 41.31; Mol.wt. 328, 329. $\text{C}_{12}\text{F}_7\text{H}_3\text{O}_3$ requires (%): C 43.90; H 0.91; F 40.55; Mol.wt. 328. On further elution with acetone, 0.9 g of a brown viscous mixture of unidentified compounds was isolated.

Oxidation of perfluoronaphthol-1 by $\text{Pb}(\text{OAc})_4$ at 20°C in acetic acid in the presence of BF_3

Boron trifluoride etherate (0.9 g) was added to a vigorously stirred suspension of $\text{Pb}(\text{OAc})_4$ (1.5 g) in acetic acid (20 ml) at 20°C. A solution of perfluoronaphthol-1 (1.0 g) in acetic acid (10 ml) was then added. NaF (5 g) was added to the solution and the latter was diluted with CCl_4 (200 ml). The solution was filtered and solvents were removed in vacuo (20 mmHg) to give a red viscous liquid (1.2 g), containing (by ^{19}F NMR) ~70% of compound VII and ~30% of compound VIII.

* Assignments of absorptions in the ^{19}F NMR spectra of compounds VII and VIII were made by comparing these spectra with those of polyfluorinated cyclohexadienones [17] and from the values of spin-spin coupling constants.

Interaction of perfluoro-1-oxo-4-(1'-naphthoxy)-1,4-dihydronaphthalene (III) with $\text{Pb}(\text{OAc})_4$

A mixture of dimer III (0.1 g) and $\text{Pb}(\text{OAc})_4$ (0.3 g) in acetic acid (20 ml) was heated at 80°C for 40 min. The solution was cooled and filtered, and acetic acid was removed under vacuum (20 mmHg). The residue was treated with 20 ml of CCl_4 and filtered. The filtrate was evaporated in vacuo. According to ^{19}F NMR and TLC analyses, the product was the initial dimer, III.

Interaction of 1-oxo-2-acetoxy-2,3,4,5,6,7,8-heptafluoro-1,2-dihydronaphthalene (VII) and 1-oxo-4-acetoxy-2,3,4,5,6,7,8-heptafluoro-1,4-dihydronaphthalene (VIII) with $\text{Pb}(\text{OAc})_2$

a) A mixture of compound VII (0.13 g) and $\text{Pb}(\text{OAc})_2$ (0.7 g) in acetic acid (10 ml) was heated at 80°C for 30 min. The mixture turned dark red and a solid precipitated. Acetic acid was distilled off in vacuo. The residue was washed with 20 ml of CCl_4 , and then treated with 30 ml of 10% HCl. The hydrochloric acid solution was extracted 5 times with 40 ml of ether. The extract was dried over CaCl_2 then evaporated in vacuo, to give 0.1 g of a pale yellow product shown by ^{19}F NMR to be 2-hydroxy-3,5,6,7,8-pentafluoro-1,4-naphthoquinone (IX).

b) Heating of compound VII in the absence of $\text{Pb}(\text{OAc})_2$ did not lead to any change in it.

c) Under similar conditions, compound VIII does not react with $\text{Pb}(\text{OAc})_2$ even during 2 h.

Oxidation of perfluoronaphthol-2 by $\text{Pb}(\text{OAc})_4$ at 20°C in ether

Perfluoronaphthol-2 (2.7 g) was added in small portions to a stirred suspension of $\text{Pb}(\text{OAc})_4$ (4.7 g) in 50 ml of absolute ether. The mixture was stirred for 1.5 h. The precipitate of lead salts was filtered and washed with 20 ml of absolute ether. The filtrate was evaporated in vacuo (20 mmHg). The residue, a yellow viscous oil, was boiled in 20 ml of hexane to remove residual lead salts and filtered. After removal of hexane by distillation, 2.5 g of the product remained; this was chromatographed on a column (200 x 2 cm) filled

with SiO_2 . Elution with CCl_4 gave 2.0 g of yellow crystalline perfluoro-2-oxo-1-(2-naphthoxy)-1,2-dihydronaphthalene (X) (nc); m.p. 134-137°C. UV spectrum, λ_{max} , nm (lg ϵ): 221 (4.88), 281 (3.84), 291 (3.81), 330 (4.12). IR spectrum, cm^{-1} : 1720m, 1690s, 1670s, 1630w, 1540s, 1500s, 1460s, 1430s, 1420s, 1370s, 1355m, 1290m, 1210m, 1180m, 1130m, 1120m, 1000m, 960s, 930s, 850m, 810m. ^{19}F NMR spectrum (50% solution in ethyl ether; ppm from C_6F_6 (internal)*): -6.6 (F^3); -8.8, -9.6 ($\text{F}^{6'}$, $\text{F}^{7'}$); -15.6, -17.0 (F^6 , F^7 , $\text{F}^{3'}$, $\text{F}^{4'}$, $\text{F}^{5'}$); -18.8, -30.7 ($\text{F}^{8'}$, $\text{F}^{1'}$, AX system, $J_{\text{peri}}^{\text{FF}}$ 66 Hz); -30.2 (F^8); -29.5, -42.2 (F^5 , F^4 , AX system, $J_{\text{peri}}^{\text{FF}}$ 78 Hz); -46.6 (F^1). the ratio of intensities was 1:1:1:2:3:1:1:1:1:1, respectively. Found (%): C 44.82, 44.51; F 49.98, 50.02; Mol.wt. 535, 539. $\text{C}_{20}\text{F}_{14}\text{O}_2$ requires (%): C 44.61; F 49.44; Mol.wt.538. Further elution with CCl_4 yielded 0.4 g of a mixture containing, according to ^{19}F NMR spectral data, ~10% of dimer X and unidentified compounds.

Oxidation of perfluoronaphthol-2 by PbO_2

Lead dioxide (4.7 g) was added in small portions over a period of 6 h to a stirred suspension of anhydrous Na_2SO_4 in a solution of perfluoronaphthol-2 (5.2 g) in dry benzene (150 ml); the reaction mixture was then stirred for an additional 8 h. The benzene solution was decanted and the precipitate was washed by decanting it 3 times with 50 ml of benzene. The benzene was distilled off in vacuo (20 mmHg). The residue was chromatographed on a column (180 x 2.2 cm) packed with SiO_2 . Elution with a 5:1 v/v hexane/benzene mixture yielded 3.0 g of dimer X. Further elution with acetone yielded 2.0 g of unidentified products.

Oxidation of perfluoronaphthol-2 by $\text{Pb}(\text{OAc})_4$ at 80°C in acetic acid in the presence of BF_3

Boron trifluoride etherate (3.2 g) was added to a vigorously stirred solution of $\text{Pb}(\text{OAc})_4$ (6.6 g) in acetic acid (50 ml) at 80°C. After that a solution of perfluoronaphthol-2 (4.1 g) in acetic acid (20 ml) was added,

* Assignments are hypothetical and made after consideration of fluorine chemical shifts in the spectra of 2-X-substituted heptafluoronaphthalenes [16] and polyfluorinated cyclohexadienones [17].

followed by NaF (15 g). The mixture was cooled to 20°C, diluted with CCl₄ (1000 ml)*, then filtered. The filtrate was evaporated in vacuo (20 mmHg), and the residue, a viscous liquid, was passed through a column (11 x 3 cm) packed with SiO₂ for complete removal of lead salts. Elution with CCl₄ gave a pale orange liquid (4.6 g) containing (by ¹⁹F NMR) ~40% of dimer X and ~60% of 2-oxo-1-acetoxy-1,3,4,5,6,7,8-heptafluoro-1,2-dihydronaphthalene (XI). The liquid was further chromatographed on a column (220 x 2.2 cm) filled with SiO₂. Elution with a 7:1 v/v mixture of CCl₄/C₆H₆ yielded 3 fractions. Fraction 1 (1.5 g): dimer X. Fraction 2 (2.6 g): pale yellow crystals of 2-oxo-1-acetoxy-1,3,4,5,6,7,8-heptafluoro-1,2-dihydronaphthalene (XI) (nc); m.p. 65.5-67.5°C. UV spectrum, λ_{max}, nm (lgε): 230 (4.23), 323 (3.97). IR spectrum, cm⁻¹: 1760s, 1730s, 1690s (C=O, -FC=CF-); 1630m, 1530s, 1500s (fluorinated aromatic ring); 1240s (acetate band). ¹H NMR spectrum (30% solution in CCl₄; δ from TMS (internal)): 2.11 (singlet) ppm. ¹⁹F NMR spectrum (30% solution in CCl₄; ppm from C₆F₆ (internal)): -6.4 (F³); -14.1 (F⁶, F⁷); -24.3, -38.9 (F⁵, F⁴, AB system, J_{peri}^{FF} 77 Hz); -26.3 (F⁸); -44.6 (F¹). The ratio of intensities was 1:2:1:1:1:1, respectively. Fluorine signals assignments were made on the basis of comparison with fluorine chemical shifts in the spectrum of perfluoro-2-oxo-1-benzoyloxy-1,2-dihydronaphthalene [18]. Fraction 3 (0.4 g): unidentified products.

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* Starting from addition of perfluoronaphthol-2, the procedures up to this point should be carried out as quickly as possible. Otherwise a sharp decrease in the yield of compound XI and the formation of its decomposition product 2-hydroxy-3,5,6,7,8-pentafluoro-1,4-naphthoquinone (IX) plus other unidentified products occurs.

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