Preliminary Note

Photochemical cyclization of polyfluorinated aryloxo-1,2-dihydronaphthalenes and 6-phenyl-3-phenoxy-2,4-cyclohexadienone

V.N. Kovtonyuk and L.S. Kobrina*

Institute of Organic Chemistry, Siberian Division, Academy of Sciences, 9 Prospekt Lavrentieva, Novosibirsk, 630090 (Russian Federation)

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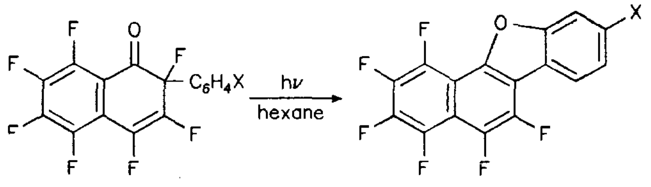
Abstract

On irradiation of solutions of polyfluorinated aryloxo-1,2-dihydronaphthalenes and 6-phenyl-3-phenoxy-2,4-cyclohexadienone, the main reaction pathway is cyclization leading to polyfluorinated benzonaphtho- and dibenzo-furans.

The photochemical behaviour of 2,4-cyclohexadienones is well known. Depending on the solvent and the structure of the starting dienone, cyclopropane derivatives or ring-cleavage products are formed [1]. 2-Oxo-1,2-dihydronaphthalenes are virtually inactive in photochemical reactions. Only one example of the cyclodimerization of such compounds is known [2]. The photolysis of substituted 1-oxo-1,2-dihydronaphthalenes leads mainly to cyclopropane derivatives [3, 4].

Polyfluorinated cyclohexadienones are convenient synthons for the selective synthesis of various fluorinated aromatic compounds, including substituted polyfluorinated phenols [5] and their derivatives [6], as well as of arylacetic acids [7]. We have now found a new photochemical method of cyclization leading to the furan derivatives from polyfluorinated aryloxo-1,2-dihydronaphthalenes and 6-phenyl-3-phenoxy-2,4-cyclohexadienone. These compounds are available by the reaction of sodium heptafluoronaphthoxides and pentafluorophenoxide with lead aryltriacetates [8].

On irradiation of hexane solutions of polyfluorinated aryloxo-1,2-dihydronaphthalenes (**Ia–c**) and phenyl-2,4-cyclohexadienone (**Id**), fluorine-containing benzonaphthofurans (**IIa–c**) and dibenzofuran (**IId**) are formed.

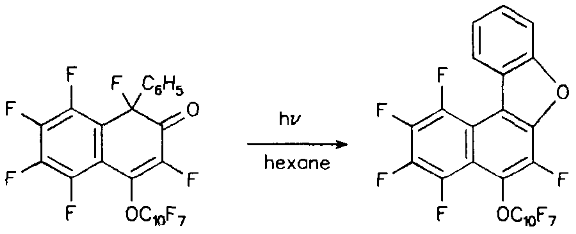


Ia X = H

Ib X = CH_3

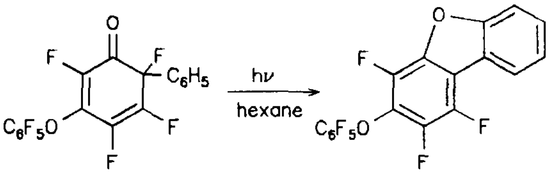
IIa 74%

IIb 69%



Ic

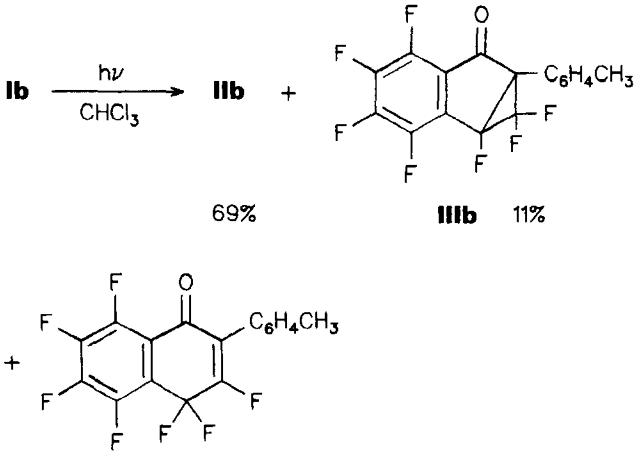
IIc 52%



Id

IId 63%

Irradiation of the chloroform solution of 2-tolyl-1-oxoheptafluoro-1,2-dihydronaphthalene (**Ib**) gave 9-methylhexafluorobenzonaphthofuran (**IIb**) as the main product, along with small amounts of products involving the migration of fluorine, 6a-tolyl-heptafluoro-1,1a-dihydrocycloprop[*a*]indenone (**IIIb**) and 2-tolyl-1-oxoheptafluoro-1,4-dihydronaphthalene (**IVb**).



69%

IIIb 11%

IVb 14%

Thus, in the case of the photochemical reactions of polyfluorinated aryl-1- and -2-oxo-1,2-dihydronaphthal-

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*Author to whom correspondence should be addressed.

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enes and 6-phenyl-3-phenoxy-2,4-cyclohexadienone, the main reaction route is cyclization to the benzonaphthofurans **IIa–c** and the dibenzofuran **IId**.

Experimental

In a typical experiment, a 1%–10% solution of the dienone (hexane, $CHCl_3$) contained in a cylindrical quartz cell was irradiated with two DRK-120 lamps equipped with a reflector, a condenser lens and a light filter (300–500 nm). Irradiation was continued until 80%–100% conversion of the starting dienone had been effected (5–50 h, TLC-Silufol UV-254 and ^{19}F NMR spectroscopic control). The temperature of the reaction mixture was ~60 °C at a maximum. The products were isolated by chromatography on an SiO_2 (100–160 μm) column (eluents: hexane, CCl_4, $CHCl_3$), and were additionally purified by sublimation. The structures of the products were established from spectral data analysis and a comparison of their UV, ^1H and ^{19}F NMR spectra with those of model compounds, i.e. benzo[*b*]naphtho[2,1-*d*]furan [9], 1,2,3,4-tetraflurodibenzofuran [10, 11] and polyfluorinated arylnaphthols [8].

*1,2,3,4,5,6-Hexafluorobenzo[*b*]naphtho[2,1-*d*]furan (**IIa**)*

On reacting 0.20 g of **Ia** for 50 h, it was possible to obtain compound **IIa** (nc) in 74% yield, m.p. 172–174 °C (in a sealed capillary). ^{19}F NMR ($CDCl_3$, δ, ppm from C_6F_6): 5.3, 6.5 (F^2, F^3); 9.1 (F^5, $J_{5,4}=61$ Hz); 16.6 (F^4); 17.9 (F^1); 18.6 (F^6). ^1H NMR ($CDCl_3$, δ, ppm, TMS): 7.48, 7.61 (H^9, H^8); 7.74 (H^{10}); 8.11 (H^7). UV (C_2H_5OH) λ_{max}, nm (log ϵ): 227 (4.28); 250 (4.57); 256 (4.80); 287 (4.15); 298 (4.18); 330 (3.71); 348 (3.84). Found: M^+, 326.0164. $C_{16}H_4F_6O$ requires: M, 326.0166.

*9-Methyl-1,2,3,4,5,6-hexafluorobenzo[*b*]naphtho[2,1-*d*]furan (**IIb**), 6a-tolyl-1,1,1a,2,3,4,5-heptafluoro-1,1a-dihydrocycloprop[*a*]inden-6(6a*H*)-one (**IIIb**), 2-tolyl-1-oxo-3,4,4,5,6,7,8-heptafluoro-1,4-dihydronaphthalene (**IVb**)*

On reacting 0.42 g of **Ib** in 12 ml of $CHCl_3$ for 40 h, it was possible to obtain 69% of **IIb**, 11% of **IIIb** and 14% of **IVb**.

Compound **IIb** (nc): M.p. 167–170 °C (in a sealed capillary). ^{19}F NMR ($CDCl_3$, δ, ppm from C_6F_6): 5.1, 7.0 (F^2, F^3); 9.2 (F^5, $J_{5,4}=61$ Hz); 16.6 (F^4); 17.9 (F^1); 18.3 (F^6). ^1H NMR ($CDCl_3$, δ, ppm, TMS): 2.56 (CH_3), 7.26 (H^8, $J_{8,7}=7.5$ Hz); 7.50 (H^{10}); 7.91 (H^7, $J_{7,8}=7.5$ Hz). UV (C_2H_5OH) λ_{max}, nm (log ϵ): 228 (4.31); 243 sh (4.35); 251 (4.58); 258 (4.77); 277 sh (4.07); 290 (4.24); 297 (4.25); 301 (4.26); 330 (3.78); 346 (3.86). Found: M^+, 340.0322. $C_{17}H_6F_6O$ requires: M, 340.0323.

Compound **IIIb** (nc): M.p. 153–157 °C (petroleum ether 40–70 °C). ^{19}F NMR ($CDCl_3$, δ, ppm from C_6F_6): -53.5 (F^{1a}); 13.4 (F^4, $J_{4,5}=20$ Hz, $J_{4,3}=17$ Hz, $J_{4,2}\sim 3.5$ Hz); 21.4 (F^3, $J_{3,2}=20$ Hz, $J_{3,4}=17$ Hz, $J_{3,5}=10.5$ Hz); 21.7 (F^2, $J_{2,3}=20$ Hz, $J_{2,5}=17.5$ Hz, $J_{2,1a}=7$ Hz, $J_{2,4}\sim$ 3.5 Hz); 22.7, 38.9 ($F^{1\alpha}$, $F^{1\beta}$, AB system, $J_{1\alpha,1\beta}=150$ Hz, $J_{1\alpha,1a}=17$ Hz, $J_{1\beta,1a}=10.5$ Hz); 26.7 (F^5, $J_{5,4}=20$ Hz, $J_{5,2}=17.5$ Hz, $J_{5,3}=10.5$ Hz, $J_{5,1a}=3.5$ Hz). ^1H NMR ($CDCl_3$, δ, ppm, TMS): 2.37 (CH_3); 7.25 (4H, C–H). UV (heptane) λ_{max}, nm (log ϵ): 220 (4.41); 251 (3.94); 290 (3.31); 300 sh (3.27). Found: M^+, 360.0380. $C_{17}H_7F_7O$ requires: M, 360.0385.

Compound **IVb** (nc): M.p. 228–231 °C ($CHCl_3$/petroleum ether 40–70 °C, 1:3). ^{19}F NMR ($CDCl_3$, δ, ppm from C_6F_6): 15.0, 18.2 (F^6, F^7); 25.0 ($F^{5,8}$); 44.9 (F^3); 60.7 (2F, F^4), ^1H NMR ($CDCl_3$, δ, ppm, TMS): 2.41 (CH_3); 7.27 (4H, C–H). UV (heptane) λ_{max}, nm (log ϵ): 221 (4.41); 259 (4.24); 291 sh (3.82); 335 (3.30). Found: M^+, 360.0402. $C_{17}H_7F_7O$ requires: M, 360.0385.

*5-(1′,3′,4′,5′,6′,7′,8′-Heptafluoro-2′-napthoxy)-1,2,3,4,6-pentafluorobenzo[*b*]naphtho[1,2-*d*]furan (**IIc**)*

On reacting 0.10 g of **1c** for 25 h, it was possible to obtain **IIc** (nc) in 52% yield, m.p. ~250 °C (with decomp. in a sealed capillary). ^{19}F NMR ($CDCl_3$, δ, ppm from C_6F_6): 4.8 (F^3); 6.2 (F^2); 7.5 ($F^{6',7'}$); 11.7 (F^6); 12.7 ($F^{3'}$); 15.8, 16.2 ($F^{4',5'}$, AB system, $J_{4',5'}\sim 55$ Hz); 16.5 ($F^{8'}$, $J_{8',1'}\sim 64$ Hz); 17.6 (F^4); 21.2 ($F^{1'}$); 23.4 (F^1). ^1H NMR ($CDCl_3$, δ, ppm, TMS): 7.53 ($H^{9,10}$); 7.71 (H^8); 8.47 (H^{11}). UV (heptane) λ_{max}, nm (log ϵ): 223 (4.87); 239 (4.76); 246 (4.79); 278 sh (4.11); 287 (4.23); 298 (4.23); 310 (4.38); 321 (4.33); 337 (4.11). Found: M^+, 576.0012. $C_{26}H_4F_{12}O_2$ requires: M, 576.0020.

*3-Pentafluorophenoxy-1,2,4-trifluorodibenzofuran (**IId**)*

On reacting 0.20 g of **Id** for 48 h, it was possible to obtain **IId** (nc) in 63% yield, m.p. 129–131 °C (in a sealed capillary). ^{19}F NMR (CCl_4+CDCl_3, δ, ppm from C_6F_6): -0.3 (F^{meta}); 1.6 (F^{para}); 3.3 (F^2, $J_{2,1}=20$ Hz, $J_{2,4}\sim 3.3$ Hz); 5.5 (F^{ortho}); 6.7 (F^4, $J_{4,1}=16$ Hz, $J_{4,2}\sim 3.3$ Hz); 15.6 (F^1, $J_{1,2}=20$ Hz, $J_{1,4}=16$ Hz). ^1H NMR (CCl_4+CDCl_3, δ, ppm, TMS): 7.39, 7.53 (H^7, H^8); 7.61 (H^6); 8.01 (H^9). UV (heptane) λ_{max}, nm (log ϵ): 218 (4.60); 245 (4.23); 255 (4.37); 277 (4.39); 291 (3.81); 303 (3.73). Found: M^+, 404.0084. $C_{18}H_4F_8O_2$ requires: M, 404.0083.

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