REACTION OF $\alpha$, $\omega$-DIOODO- AND $\alpha$, $\beta$-DICHLORO-$\omega$-IODOPERFLUOROALKANES WITH SOME AROMATIC COMPOUNDS

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When $\omega$-iodo-$\alpha$, $\beta$-dichloroperfluoroalkanes were reacted with benzene we obtained the corresponding dichloroperfluoroalkylbenzenes [1].

$$
(CF_2)_n CFCI + NCI \rightarrow (CF_2)_n CFCI - CF_2Cl
$$

In the present paper it was shown that the heating of benzene with $\alpha$, $\omega$-diiodoperfluoroalkanes, like 1,2-diiodoperfluoroethane and 1,6-diiodoperfluorohexane, leads to the respective formation of 1,2-diphenylperfluoroethane and 1,6-diphenylperfluorohexane.

The alkylation of benzene with 1,2-diiodoperfluoroethane gave, besides 1,2-diphenylperfluoroethane, 1-hydro-2-phenylperfluoroethane, perfluorocyclobutane and a small amount of 1,2-dihydroperfluoroethane. The formation of perfluorocyclobutane is apparently explained by the thermal instability of 1,2-diiodoperfluoroethane.

In contrast to 1,2-diiodoperfluoroethane and 1,6-diiodoperfluorohexane, 1,4-diiodoperfluorobutane reacts with benzene to form 1,1,2,2,3,3,4,4-octafluorotetralin, the structure of which was confirmed by its defluorination with iron turnings at 500°C to give 1,2,3,4-tetrafluoronaphthalene* [2, 3].

The alkylation of naphthalene and bromobenzene with $\alpha$, $\omega$-diiodoperfluoroalkanes and 1,2-dichloro-4-iodoperfluorobutane goes in a similar manner.

The infrared spectrum of the alkylation product of bromobenzene with 1,2-dichloro-4-iodoperfluorobutane the most intense absorption bands were detected at 703, 731 and 781 cm$^{-1}$, of which the bands at 703 and 781 cm$^{-1}$ correspond to the $m$-substituted isomer, while the band at 731 cm$^{-1}$ can belong to the $o$-substituted isomer, and the band at 809 cm$^{-1}$, of medium intensity, can correspond to the $p$-substituted isomer [4].

*We were granted Author's Certificate a form of Russian Patent No. 170,932 for the method of preparing 1,2,3,4-tetrafluoronaphthalene.

The consecutive alkylation of diphenyl ether with 1,2-dichloro-8-iodoperfluorooctane gave the mono- and disubstituted diphenyl ethers. The dechlorination of 1,2-dichloro-8-phenoxyphenylperfluorooctane with zinc in acetic acid gave the corresponding olefin.

![Chemical structure](image)

The alkylation of diphenyl ether with 1,6-diiodoperfluorohexane gave 1,6-bis(phenoxyphenyl)perfluorohexane.

![Chemical structure](image)

**EXPERIMENTAL**

*Reaction of Benzene with 1,2-Diiodoperfluoroethane.* Into a steel ampule were charged 106.2 g of 1,2-diodoperfluoroethane, 100 ml of benzene and 78 g of sodium acetate. With shaking, the ampule was heated for 8 h at 250°. Then the ampule was cooled and 7.2 g of a low-boiling liquid was collected in a trap, the composition of which, based on the gas-liquid chromatographic (GLC) data, corresponded to 3% of 1,2-dihydroperfluoroethane and 97% of perfluorocyclobutane (11.6% yield when based on 1,2-diiodoperfluoroethane). The ampule contents were washed with sodium hyposulfite solution, then with water, and dried over MgSO₄. After distilling off the benzene we obtained: a) 12.6 g (23.59%) of 1-hydroxy-2-phenylperfluoroethane, bp 69-70° (60 mm), nD₂⁰ 1.4240; d₄₂⁰ 1.2900. Found %: C 52.98; H 3.30; F 42.57; MR 35.21. C₉H₆F₄. Calculated %: C 53.93; H 3.37; F 42.70; MR 35.55 (AR F = 1.1). From the data given in [5, 6]: bp 68° (60 mm); nD₂⁰ 1.4258; d₄₂⁰ 1.27, and b) 19 g (24.9%) of 1,2-diphenylperfluoroethane, mp 124-125° (from ethanol). From the data given in [7]: mp 122°.

*1,6-Diphenylperfluorohexane.* In a similar manner, from 28 g of 1,6-diiodoperfluorohexane, 80 ml of benzene and 20 g of sodium acetate we obtained 7.5 g (33%) of 1,6-diphenylperfluorohexane, bp 172-173° (15 mm); nD₂⁰ 1.4360; d₄₂⁰ 1.507. Found %: C 47.19; H 2.17; F 51.02; MR 78.77. C₁₈H₁₀F₁₂. Calculated %: C 47.58; H 2.20; F 50.22; MR 79.12.

*1,1,2,2,3,3,4,4-Octafluorotetralin.* In a similar manner, from 45.4 g of 1,4-diiodoperfluorobutane, 100 ml of benzene and 40 g of sodium acetate we obtained 29 g (72.5%) of 1,1,2,2,3,3,4,4-octafluorotetralin, bp 90° (42 mm); nD₂⁰ 1.4030; d₄₂⁰ 1.516. Found %: C 43.52; H 1.72; F 55.05; MR 44.43; mol. wt. 281. C₁₈H₁₀F₂₄. Calculated %: C 43.50; H 1.45; F 55.05; MR 43.72; mol. wt. 276.

*1,2,3,4-Tetrafluoronaphthalene.* Through a quartz tube, with a length of 40 cm and a diameter of 7 mm, filled with iron turnings, at 500°, were passed the vapors of 1,1,2,2,3,3,4,4-octafluorotetralin. At the other end of the tube, the liquid and crystals were condensed in a cooled receiver. The liquid was again passed through the tube filled with iron turnings. The crystals were sublimed and then recrystallized from ethyl alcohol. The 1,2,3,4-tetrafluoronaphthalene had mp 106-108°. From [2, 3]: mp 110-111°. Found %: C 60.38; H 2.00; F 38.18. C₁₈H₁₄F₄. Calculated %: C 60.00; H 2.00; F 38.00.

*1,2-Dinaphthylperfluoroethane.* Into a 250-ml steel autoclave were charged 51.2 g of naphthalene, 71 g of 1,2-diiodoperfluoroethane and 54 g of sodium acetate. With shaking, the autoclave was heated for 8 h at 250°. The reaction mixture was dissolved in a mixture of ether and chloroform, washed with sodium hyposulfite solution, then with water, and dried over MgSO₄. After distilling off the solvents and the unreacted naphthalene (~12 g) we obtained 15 g of a liquid, bp 98-139° (5 mm), and 13 g of a very viscous mass, bp 200-223° (0.01 mm). Redistillation of the first liquid failed to give any pure compounds; the viscous mass crystallized. After washing the material with petroleum ether and recrystallization from dioxane we obtained 7.2 g of 1,2-dinaphthylperfluoroethane (10% yield), mp 188-189°. Found %: C 74.56; H 4.04; F 21.33. C₂₂H₂₄F₄. Calculated %: C 74.58; H 3.95; F 21.47.