Chemistry

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Abstract

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SOME REACTIONS OF DECAFLUORODIPHENYL

Decafluorodiphenyl has previously been obtained by fluorination of diphenyl with CoF_3, followed by dehalogenation of polyfluoro derivatives of dicyclohexyl (^{1}), by the Ullmann reaction from pentafluorobromobenzene (^{2}), and also by the action of KF on decachlorodiphenyl (^{3}). Recently a report appeared on the preparation of decafluorodiphenyl from pentafluorochlorobenzene by the Ullmann method in 69% yield (230°, 280 h) (^{4}). We have shown that under more severe conditions (360°) the reaction proceeds considerably faster and decafluorodiphenyl is obtained in 75% yield. Owing to the ease of preparation of pentafluorochlorobenzene (^{5}), decafluorodiphenyl has thus become an accessible product, which made it possible to study some of its reactions. It was found that nucleophilic substitution of fluorine atoms occurs exclusively in the 4,4′-positions.

On treatment of decafluorodiphenyl with 30% aqueous ammonia, octafluorobenzidine is obtained; its structure is proved by the presence in the ^{19}F NMR spectrum of two bands of equal intensity. Octafluorobenzidine is readily diazotized in a mixture of acetic and sulfuric acids. The use of hydrochloric acid instead of sulfuric acid leads to replacement of 3–4 fluorine atoms by chlorine. Coupling of the bisdiazo compound with β-naphthol and naphthionic acid gave the corresponding dyes. The UV spectrum of the fluorinated analogue of Congo red is similar to the UV spectrum of Congo red. However, the dye does not change color in an acidic medium.

Oxidation of octafluorobenzidine with trifluoroperacetic acid gave 4,4′-dinitro-octafluorodiphenyl.

Reaction of decafluorodiphenyl with an alcoholic solution of hydrazine hydrate gave 4,4′-bishydrazino-octafluorodiphenyl. The position of the hydrazino groups is proved by the fact that on reduction with hydroiodic acid this product is converted into octafluorobenzidine. Treatment with Fehling’ s solution leads to the formation of 2,2′-, 3,3′-, 5,5′-, 6,6′-octafluorodiphenyl.

Heating decafluorodiphenyl with an aqueous-alcoholic solution of dimethylamine gave 4,4′-bisdimethylamino-octafluorodiphenyl. This compound is identical with the product obtained by treatment of octafluorobenzidine with methyl ester of *p*-toluenesulfonic acid.

On treatment of decafluorodiphenyl with KOH in tert-butyl alcohol, 4,4′-dioxyoctafluorodiphenyl was obtained. The ^{19}F NMR spectrum of this compound has one split band, which is possible only when the hydroxy groups are located in the 1,4′-positions. It had previously been stated (^{6}) that hexafluorobenzene is insensitive to oxygen-containing nucleophilic reagents in aqueous medium. We found that, under the action of a 5% aqueous KOH solution, decafluorodiphenyl is converted in good yield into 4,4′-dioxyoctafluorodiphenyl.

In the IR spectrum of 4,4′-dioxyoctafluorodiphenyl in KBr there is an absorption band in the region of 3250 cm^{-1}, characteristic of an intramolecular hydrogen bond H···F. The correctness of assigning this band is confirmed by the fact that it is not observed in the IR spectrum of the nonfluorinated analogue. Absorption bands in the region of 3475 and 3550 cm^{-1} in KBr, characteristic of intermolecular hydrogen bonds, are observed both in the spectrum of 4,4′-dioxydiphenyl and in the spectrum of its fluorinated analog. The IR spectrum of 4,4′-dioxyoctafluorodiphenyl, recorded in CCl_4, contains no bands characteristic of intermolecular hydrogen bonds, while the band in the region of 3250 cm^{-1} is somewhat weakened, probably owing to solvation.

With sodium methylate in methanol, decafluorodiphenyl reacts with formation of 4,4′-dimethoxyoctafluorodiphenyl, which proved to be identical with the product obtained by treating 4,4′-dioxyoctafluorodiphenyl with diazomethane.

The UV spectra of fluorinated diphenyl derivatives (see Table 1) are cha—

Table 1

UV spectra of polyfluoro derivatives of diphenyl

Compound	Solvent	λ_max (lg ϵ)	Source
Decafluorodiphenyl	Petroleum ether	226—228 (4.14)264—266 (3.32)	
Octafluorodiphenyl	Same	228 (4.19)272 (3.66)	
Diphenyl	»	248 (4.23)	(7)
Octafluorobenzidine	Methanol	266—268 (4.45)	
2,2′-, 6,6′-Tetrafluorobenzidine	Same	262 (4.45)	(8)
Benzidine	»	282—286 (4.40)	(8)
4,4′-Dinitrooctafluorodiphenyl	Ethanol	250—256 (4.23)	
4,4′-Dinitrodiphenyl	Same	306 (4.40)	(9)
4,4′-Dioxyoctafluorodiphenyl	»	268—272 (4.40)	
4,4′-Dioxydiphenyl	»	264—266 (4.34)	

Compound	Solvent	λ_max (lg ϵ)	Source
Fluorinated analog of Congo red	0.1 N aqueous NaOH	228–244 (4.48)332–346 (4.43)470–496 (4.53)	
Congo red	Same	224–226 (5.02)296–298 (4.46)468–494 (3.87)	

–racterized by a shift of the absorption maximum into the short-wavelength region in comparison with the spectra of the corresponding compounds that do not contain fluorine. This is apparently due to a certain disturbance of the coplanarity of the benzene rings as a result of steric hindrance caused by the presence of fluorine atoms in the 2,2′ and 6,6′ positions, as is consistent with the closeness of the UV spectrum of octafluorobenzidine to the spectrum of 2,2′-,6,6′-tetrafluorobenzidine. In addition, in the spectra of fluorine-substituted diphenyls an absorption maximum of lower intensity appears in the long-wavelength region. The changes in the UV spectrum of diphenyl associated with the introduction of fluorine atoms agree well with data on the UV spectra of 2-fluoro- and 2,2′-difluorodiphenyls (10).

Experimental Part

Decafluorodiphenyl (I). 2.5 g of C_6F_5Cl and 8 g of copper bronze are heated in a sealed tube for 40 h at 320–360°. The reaction product is extracted with ether. Steam distillation gives 1.52 g (73%) of I. M.p. 67.5–68° (from petroleum ether). According to (1), m.p. 67–69°. The IR spectrum coincides with the IR spectrum of the product obtained according to (3).

Octafluorobenzidine (II). 1.2 g of I and 120 ml of 30% aqueous NH_3 are heated in an autoclave for 6 h at 130°. 0.82 g of II is filtered off. M.p. 173–174° (from petroleum ether). Extraction of the filtrate with ether gives an additional 0.2 g of II. Overall yield 91%.

Found, %:	N 8.6; 8.7;	F 46.0; 46.2
$C_{12}H_4F_8N_2$. Calculated, %:	N 8.5;	F 46.3

IR spectrum (in KBr): 1500, 1520 cm^{-1} (fluorinated aromatic ring); 3200, 3340, 3440, 3455 cm^{-1} (NH). Bisacetyl derivative; mp 367-368°.

Found, %:	N 6.8; 6.8;	F 36.2; 36.3
$C_{16}H_8F_8N_2O_2$. Calculated, %:	N 6.8;	F 36.9

4,4′-Bishydrazino-octafluorodiphenyl (III). 1 g of I, 6 ml of 100% hydrazine hydrate, 12 ml of alcohol, and 1.5 ml of water are boiled for 16 h. 0.8 g of III is filtered off. Golden plates with mp 208–209° (from alcohol). From the filtrate, extraction with CH_2Cl_2 gives a further 0.3 g of III. Overall yield 78%.

Found, %: N 15.3; 15.6; F 42.5; 42.8
$C_{12}H_6F_8N_4$. Calculated, %: N 15.6; F 42.4

IR spectrum (in KBr): 1500, 1535 cm^{-1} (fluorinated aromatic ring); 3275, 3380, 3405 cm^{-1} (NH). Treatment with benzaldehyde gives the bishydrazone with mp 240–241.5° (from alcohol).

Found, %: N 10.9; 11.0
$C_{26}H_{14}F_8N_4$. Calculated, %: N 10.5

By reducing 0.25 g of III with 10 ml of 55% HI, 0.12 g of II is obtained, identical with the product described above.

Octafluorodiphenyl (IV). 0.6 g of III is boiled with an excess of Fehling’s solution. Steam distillation gives 0.28 g (52%) of IV. Mp 82–83.5° (from petroleum ether).

Found, %: C 48.2; 48.3; H 0.7; 0.9; F 50.9; 51.0
$C_{12}H_2F_8$. Calculated, %: C 48.3; H 0.7; F 51.0

IR spectrum (in KBr): 1500, 1520 cm^{-1} (fluorinated aromatic ring); 3070 cm^{-1} (C—H stretching vibrations); 860, 920 cm^{-1} (out-of-plane C—H deformation vibrations).

4,4′-Bis-dimethylamino-octafluorodiphenyl (V). 0.2 g of I, 10 ml of 33% aqueous dimethylamine, and 10 ml of alcohol are heated for 3 h at 80°. 0.18 g (86%) of V is filtered off. Mp 107–108° (from alcohol).

Found, %: N 7.4; 7.5; F 39.0; 39.3
$C_{16}H_{12}F_8N_2$. Calculated, %: N 7.3; F 39.3

IR spectrum (in KBr): 1490, 1530 cm^{-1} (fluorinated aromatic ring); 2820, 2860, 2900, 2940 cm^{-1} (CH_3).

Azo dye from octafluorobenzidine. To a solution of 0.5 g of II in a mixture of 15 ml of glacial CH_3COOH and 7.5 ml of H_2SO_4, cooled to 5°, 0.24 g of dry $NaNO_2$ is added. The light-yellow solution is filtered and added dropwise to a solution of 0.4 g of β-naphthol in 2 ml of 5% aqueous KOH. 0.7 g of red crystals is filtered off. Mp 310–311.5° (from alcohol).

Found, %: N 8.9; 8.9; F 23.9; 23.9
$C_{32}H_{14}F_8N_4O_2$. Calculated, %: N 8.8; F 23.8

By coupling a solution of the bis-diazo compound from 0.5 g of II with an alkaline solution of 0.5 g of naphthionic acid, 0.95 g of a fluorinated analog of Congo red is obtained.

4,4′-Dinitro-octafluorodiphenyl (VI). 10 ml of CH_2Cl_2, 2.5 ml of trifluoroacetic anhydride, and 1 ml of 90% H_2O_2 are boiled for 20 min, after which a solution of 0.5 g of II in 10 ml of CH_2Cl_2 is slowly added. The mixture is boiled for 2 h, 0.5 ml of H_2O_2 and 0.5 ml of trifluoroacetic anhydride are added. After 20 h of boiling, 20 ml of water is added and the mixture is stirred for 20 min. The lower layer is separated, washed with water, and dried over $MgSO_4$. The CH_2Cl_2 is distilled off, giving 0.5 g (86%) of VI. Mp 83-84.5° (from petroleum ether).

Found, %:	N 7.5; 7.6; F 39.0; 39.2
$C_{12}F_8N_2O_4$. Calculated, %:	N 7.2; F 39.2

IR spectrum (in KBr): 1500, 1520 cm^{-1} (fluorinated aromatic ring); 1370, 1571 cm^{-1} (NO_2).

4,4′-Dihydroxyoctafluorodiphenyl (VII). a) 1 g of I, 1.5 g of KOH, and 20 ml of tert-C_4H_9OH are boiled for 1 h. To the cooled mixture, 25 ml of water is added and the alcohol is distilled off. The aqueous residue is filtered and extracted with ether. After extraction, the aqueous layer is acidified with 6 N HCl and again extracted with ether. The last ether extract is washed with water, dried with $MgSO_4$. The ether is distilled off in vacuo. 0.67 g (68%) of VII is obtained, with m.p. 198.5-199.5° (from benzene).

Found, %: C 43.5; 43.7; H 0.6; 0.8; F 45.0; 45.2
$C_{12}H_2F_8O_2$. Calculated, %: C 43.6; H 0.6; F 46.0

IR spectrum (in KBr): 1500, 1525 cm^{-1} (fluorinated aromatic ring); 3270 cm^{-1} (intramolecular hydrogen bond); 3475 and 3550 cm^{-1} (intermolecular hydrogen bond); 3655 cm^{-1} (OH).

b) 1 g of I and 130 ml of 5% aqueous KOH solution are heated for 7.5 h at 160°. 0.15 g of I is filtered off; the filtrate is acidified with 5 N HCl to pH $\sim$ 2. The precipitated crystals are filtered off. 0.72 g (85%) of VII is obtained, with m.p. 198-199.5°.

4,4′-Dimethoxyoctafluorodiphenyl (VIII). 0.2 g of I is boiled for 6 h with a solution of 0.15 g of Na in 15 ml of absolute methanol. 100 ml of water is added; 0.18 g (86%) of VIII is filtered off, with m.p. 83-84.5° (from alcohol).

Found, %: C 47.3; 47.4; H 1.8; 1.9; F 42.5; 42.8
$C_{14}H_6F_8O_2$. Calculated, %: C 47.0; H 1.7; F 42.4

IR spectrum (in KBr): 1485, 1500, 1520 cm^{-1} (fluorinated aromatic ring); 2850, 2900, 2960, 2970, 3020 cm^{-1} (CH_3).

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CITED LITERATURE

1. B. Gething, C. Patrik et al., *Nature*, **183**, 588 (1959).
2. E. Nield, R. Stephens, J. Tatlow, *J. Chem. Soc.*, **1959**, 166.
3. G. G. Yakobson, V. D. Shteingarts, N. N. Vorozhtsov, Jr., *Izv. AN SSSR, ser. khim.*, **1964**, 1551.
4. G. Brooke, R. Chambers et al., *J. Chem. Soc.*, **1964**, 729.
5. N. N. Vorozhtsov, Jr., V. E. Platonov, G. G. Yakobson, *Izv. AN SSSR, ser. khim.*, **1963**, 1524.
6. J. Birchall, R. Haszeldine, *J. Chem. Soc.*, **1959**, 13.
7. G. Beaven, E. Jonson, *Spectrochim. acta*, **15**, 67 (1959).
8. R. Carlin, S. Heininger, *J. Am. Chem. Soc.*, **77**, 2272 (1955).
9. R. Sandin, R. Melbi et al., *J. Am. Chem. Soc.*, **74**, 5073 (1952).
10. G. H. Beaven, D. Hall, *J. Chem. Soc.*, **1957**, 4637.

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