Journal of Fluorine Chemistry, 8 (1976) 193–207
© Elsevier Sequoia S.A., Lausanne – Printed in the Netherlands
Received: July 9, 1975

AROMATIC FLUORO DERIVATIVES.
LXX. INTERACTION OF PENTAFLUOROBENZOYL PEROXIDE WITH DECAFLUORODIPHENYL

L.S. KOBRINA, V.L. SALENKO and G.G. YAKOBSON

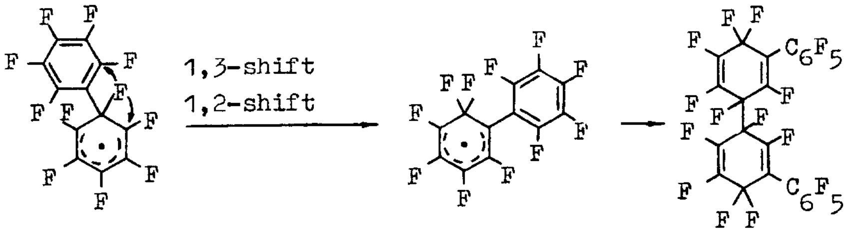
Institute of Organic Chemistry, 630090, Novosibirsk (U.S.S.R.)

SUMMARY

The interaction of pentafluorobenzoyl peroxide with decafluorodiphenyl (at 80°C and 200°C) results in the preferential formation of perfluorotetrakisphenyl-tetrahydrodiphenyls (a mixture of isomers). Defluorination of perfluoro-3,3',5,5'-tetrakisphenyl-1,1',2,2'-tetrahydrodiphenyl-1,1' gives rise to perfluoro-3,3',5,5'-tetrakisphenyldiphenyl-1,1'. The results obtained confirm the proposition about the 1,2-shift of the fluorine atom in the initial σ-complex formed by the addition of the pentafluorophenyl radical to decafluorodiphenyl.

INTRODUCTION

On investigating the reaction of pentafluorobenzoyl peroxide and hexafluorobenze (at 200°C) we have found that the initially formed radical σ-complex appears to rearrange by migration of the fluorine atom. This results in a more stable radical σ-complex [1]. However, this reaction does not distinguish between the two possible pathways of fluorine atom migration, i.e. to a neighbouring position in the same ring or to a neighbouring ring (1,2- or 1,3-shift, respectively), since in both cases the structure of the rearranged σ-complex should be the same.



(I)

It has been proposed that the rearrangement is of a general character and that fluorine atom migration is possible in the σ-complex formed when the phenyl radical attacks hexafluorobenzene. In this case the structure of the dimerization products of the σ-complexes should depend significantly on the pathway of the fluorine atom migration in the initial σ-complex. Isomeric bisphenylperfluorotetrahydrodiphenyls have been isolated when hexafluorobenzene reacts with benzoyl peroxide at 80°C. Defluorination of this mixture yields 3,4'-bis(phenyl)octafluorodiphenyl and 4,4'-bis(phenyl)octafluorodiphenyls. The structure of the preferentially formed 3,4'-bis(phenyl)octafluorodiphenyl suggests that rearrangement of the initially formed σ-complex is effected probably by means of a 1,2-shift of the fluorine atom.

RESULTS AND DISCUSSION

In the present paper the reaction of decafluorodiphenyl (DFD) with pentafluorobenzoyl peroxide is described. This has allowed the study of both the mechanism of the rearrangement and the effects of substituents on the stereochemistry of pentafluorophenylation of polyfluoroaromatic compounds.

Perfluoroterphenyls and a mixture of products of formula $C_{36}F_{30}$ have been isolated from the products of the reaction of decafluorodiphenyl with pentafluorobenzoyl peroxide (at 80°C and 200°C). The $C_{36}F_{30}$ compounds appear to consist of a mixture of isomeric perfluorotetrakis(phenyl)tetrahydrodiphenyls - dimers of the radical σ-complexes which result from the addition of the pentafluorophenyl radical to DFD.

The yields of these dimers and perfluoroterphenyls, as well as the isomeric composition of the latter under various reaction conditions, are given in Table 1.

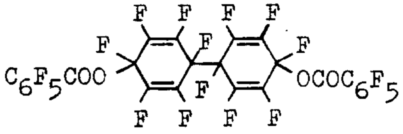
TABLE 1

Reaction of pentafluorobenzoyl peroxide and DFD (yields in moles per mole of peroxide)

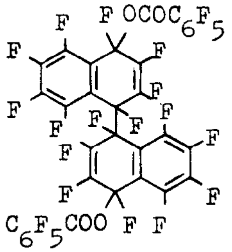
Temperature (°C)	Time (hrs)	Peroxide concentr. (mole)	Yield of dimers[a]	Yield of perfluoroterphenyls	Isomeric perfluoroterphenyls O : m : p
80	40	1.0	0.60	0.11	1.0 : 4.6 : 2.1
80	40	0.5	0.48	0.09	1.0 : 3.3 : 2.1
200	5	1.0	0.59	0.26	1.0 : 1.7 : 1.2
200	5	0.5	0.54	0.27	1.0 : 1.5 : 1.5

[a] Yields of dimers are given in terms of the isolated products.
[b] Yields of perfluoroterphenyls calculated from GLC analyses.
[c] The amounts of the components were determined by comparison with known weights of added authentic samples; calibration graphs were employed to compare the response of the instrument towards the various compounds.

The data presented in Table 1 show that of the two possible pathways for the reaction between pentafluorobenzoyl peroxide and DFD-homolytic substitution of the fluorine atoms and dimerization of the radical σ-complexes — the second is predominant. Preferential formation of dimers in the reactions of pentafluorobenzoyl peroxide with hexafluorobenzene [1] and octafluoronaphthalene [3] have been observed earlier. However, reactions at 80°C give rise to dimers of the σ-complexes resulting from the addition of two pentafluorobenzoyloxy radicals — compounds (II) and (III), respectively.



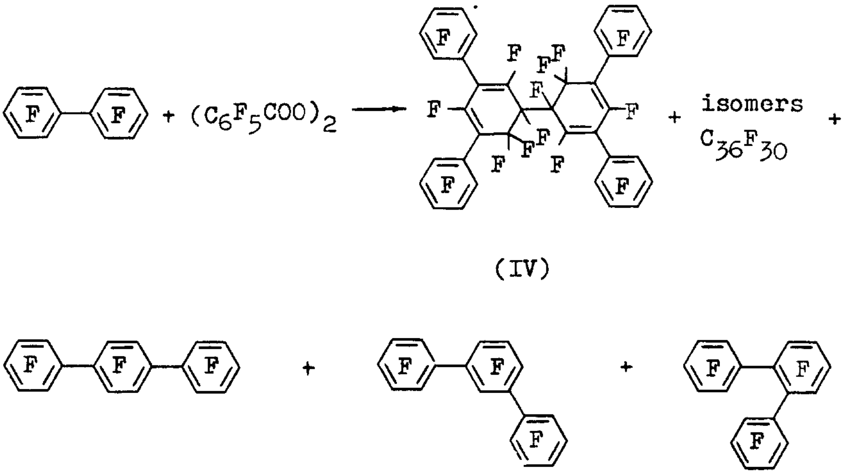
(II)



(III)

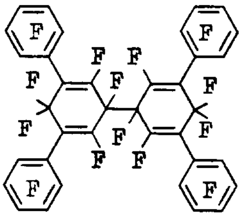
The absence of dimers of this type in the products of the reaction of pentafluorobenzoyl peroxide and DFD at 80°C may be attributed to their lower thermal stability. If both the formation of such dimers and the formation of the respective σ-complexes are reversible [1, 3] , under the reaction conditions employed, decomposition may occur leading to the initial DFD an the pentafluorobenzoyloxy radical, which is then decarboxylated and eliminated from the reaction.

An individual dimer isolated was identified as perfluoro-3,3',5,5'-tetrakisphenyl-1,1',2,2'-tetrahydrodiphenyl-1,1' (IV) on the basis of IR and ^{19}F NMR spectra.

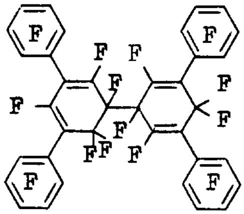


(IV)

The ^{19}F NMR spectrum of compound (IV) (20% solution in nitrobenzene at 160°C contains seven signals: +5.6, -1.8, -16.3, -28.6, -58.1, -72.2 and -77.3 ppm of 2:8:4:8:4:2:2 intensity, respectively. The signals corresponding to the chemical shifts -1.8, -16.3 and -28.6 ppm may be attributed to the m-, p- and o-atoms of the fluorine in the four pentafluorophenyl rings, the signal at +5.6 ppm to the 1,1'-fluorine atoms [1] and the signal at -58.1 ppm to the fluorine atoms associated with the double bond (2,4,2',4'). The signals at -72.2 and -77.3 ppm of the fluorine atoms of the CF_2 groups form an AB system with J_{gem}^{FF} = 300 Hz. The IR spectrum of (IV) exhibits strong bands at 1500 cm^{-1} (perfluorinated aromatic ring) and at 1730 cm^{-1} (fluorinated double bond). The frequency of the fluorinated double bond makes it possible to identify compound (IV) as perfluoro-3,3',5,5'-tetrakis(phenyl)-1,1,2,2-tetrahydrodiphenyl rather than its isomers (V) and (VI) (the ^{19}F NMR spectra of all the isomers should be similar), since it is known that in perfluoro-2-phenylcyclohexa-1,3-diene the frequency of the double bonds is at 1740 cm^{-1} and in perfluoro-2-phenylcyclohexa-1,4-diene at 1780 cm^{-1} [4] .

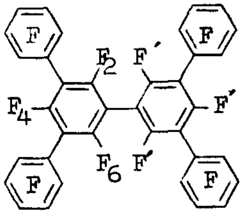


(V)



(VI)

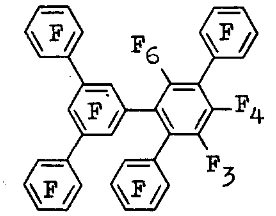
Defluorination of (IV) with zinc dust in glacial acetic acid yields perfluoro-3,3',5,5'-tetrakisphenyldiphenyl-1,1' (VII)



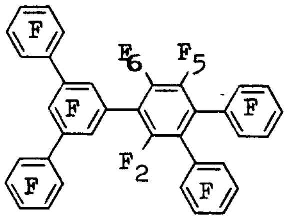
(VII)

The ^{19}F NMR spectrum of compound (VII) (20% nitrobenzene solution at 180°C consists of four signals with chemical shift values of -1.6, -11.4, -25.0 and -60.7 ppm respectively, and with the intensity ratio 8:4:8:6. The signals at -1.6, -11.4 and -25.0 ppm may be attributed, respectively, to the m-, p- and o-fluorine atoms in the pentafluorophenyl groups and the signal a -60.7 ppm to the fluorine atoms of the 2,2',4,4',6,6'-substituted aromatic rings. Calculations of the chemical shift values for these fluorine atoms using increments for the C_6F_5 group yield a value of -60.0 ppm [5].

The mixture of isomeric perfluorotetrakis(phenyl)tetrahydrodiphenyls (after separation of compound (IV)) was defluorinated to give the isomeric perfluorotetrakis(phenyl)diphenyls. The latter seems to be a mixture of compounds (VIII) and (IX). The ^{19}F NMR spectrum of this mixture (25% solution in CCl_4) consists of six signals with chemical shifts at -1.8, -12.4, -25.4, -36.4, -51.0 (broadened) and -60.7 ppm with the intensity ratio 8:4:9:1:1:3, respectively. The signals at -1.8 and -12.4 ppm may be attributed to the m- and p-fluorine atoms in the pentafluorophenyl groups, while the presence of o-fluorine atoms in these groups increases the intensity of the signal at -25.4 ppm eight times. The presence of the signal at -60.7 ppm of intensity 3 suggests the existence of a 1,3,5-tri-substituted ring (cf. the ^{19}F NMR spectrum of compound (IV)). The presence in the spectrum of three more signals of equal intensity may indicate that the remaining fluorine atoms are not equivalent. Calculations of the chemical shifts of the fluorine atoms in the asymmetrically substituted ring of compounds (VIII) and (IX) using the increments for the C_6F_5 group give values close to the experimentally determined ones: $F_{6(2)}$, -49.5; $F_{4(6)}$, -37.5; $F_{3(5)}$, -27.0 ppm.

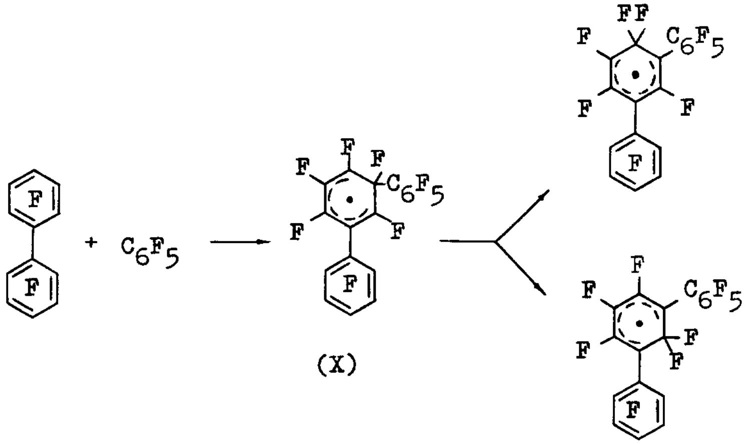


(VIII)

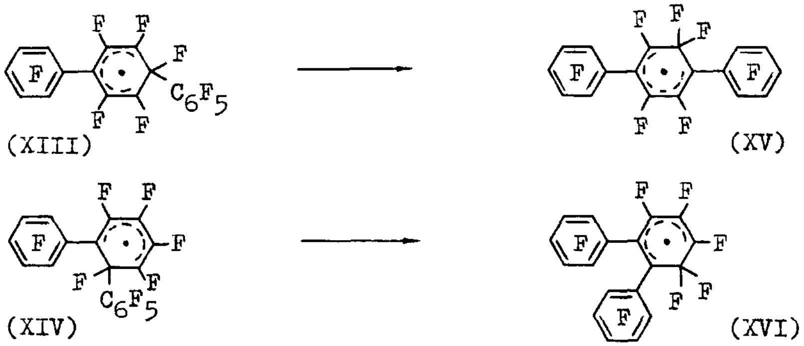


(IX)

The following scheme may be proposed for the reaction between DFD pentafluorobenzoyl peroxide. The pentafluorophenyl radical attacks the metaposition of the DFD molecule giving rise to the σ-complex (X·) which, following a 1,2-migration of the fluorine atom, rearranges to give the σ-complexes (XI) and (XII)



The pentafluorophenyl radical attacks the para and ortho positions of DFD to give the σ-complexes (XIII) and (XIV) which can rearrange following a 1,2-shift of the fluorine atom to form the σ-complexes (XV) and (XVI), respectively.



It should be noted that if the driving force for the rearrangement is the possibility of participation of the pentafluorophenyl ring in the delocalization of the density of the unshared electron, then the σ-complexes (XIII) and (XIV) would not apparently be subject to such a rearrangement. In both rearranged complexes (XV) and (XVI) and in the unrearranged complexes (XIII) and (XIV) one of two pentafluorophenyl rings can participate in delocalization. The structure of the products formed does not provide a sound basis for conclusions regarding the course of the rearrangement of the σ-complexes (XIII) and (XIV) since when the σ-complexes (XI) and (XII) react with the σ-complexes (XIII), (XIV), (XV) and (XVI), 10 isomeric perfluorotetrakis(phenyl)tetrahydrodiphenyls can arise which on defluorination should yield only the compounds (VIII) and (IX).

Stabilization of the σ-complexes formed can come about in several ways: defluorination (disproportionation) yields perfluoroterphenyls (this problem is discussed below) and dimerization (recombination) yields isomeric perfluorotetrakis(phenyl)-tetrahydrodiphenyls. As mentioned above, the latter is the predominant process (Table 1). The structure and proportion of the products formed indicate that the main role in the formation of all the reaction products is played by the σ-complexes (XI) and (XII). This suggests that the concentration and, apparently, the stability of the σ-complexes (XI) and (XII) are considerably higher than the concentration and stability of their isomers.

The stability of the σ-complex (XI) is, probably, higher and its high stationary concentration results in the formation of its dimerization product - compound (IV).

The less stable σ-complexes (XIII), (XIV), (XV) and (XVI) are present in the mixture in lower concentrations, and are not dimerized but recombine with the σ-complexes (XI) and (XII).

The results obtained suggest that the pentafluorophenyl radical appears to preferentially attack the metaposition in DFD and the σ-complex formed during this process rearranges via 1,2-migration of the fluorine atom.

The high reactivity of the metaposition in DFD is somewhat unexpected since it could be assumed that of the initially formed σ-complexes the most stable are those in which the pentafluorophenyl group is in positions which allow it to participate in the delocalization of the density of the unshared electron ((XIII) and (XIV)). Most probably the stability of the fluorinated σ-complexes depends on factors which cannot be evaluated on the basis of the data obtained.

Despite the comparatively small contribution of homolytic substitution during the course of the reaction of DFD with pentafluorobenzoyl peroxide, it is of some interest to discuss the data on the isomeric composition of the perfluoroterphenyls formed and to compare them with the results of similar reactions involving the non-fluorinated series in order to evaluate the effect of the presence of fluorine atoms on the reactivity of the diphenyl.

The data presented in Table I demonstrate that a variation in the temperature of the reaction between pentafluorobenzoyl peroxide and DFD affects both the yield and the isomeric distribution of perfluoroterphenyls. An increase in the yield of these products may be attributed to the more ready defluorination of the respective σ-complexes with increasing temperature while the isomeric composition of the perfluoroterphenyls obtained at 200°C reflects the decreasing selectivity of the pentafluorophenyl radical under more drastic reaction conditions.

The ratios of the isomeric terphenyls obtained by phenylation and pentafluorophenylation of diphenyl and pentafluorophenylation of DFD are presented in Table 2.

TABLE 2

Ratios of isomeric terphenyls formed by arylation of diphenyls

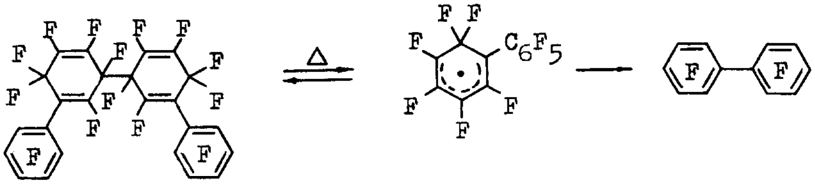
Diphenyl	Radical source	Temperature (°C)	Ratios of isomers (%)			O + P : M ratios
			O	P	M	
	$(C_6H_5COO)_2$ [a]	80	48	29	23	3.6
$C_{12}H_{10}$	C_6F_5J [b]	80	24	39	37	1.7
	$(C_6F_5COO)_2$	200	24	30	46	1.2
$C_{12}F_{10}$	$(C_6F_5COO)_2$	80	13	27	60	0.7

[a] See Ref. 6.

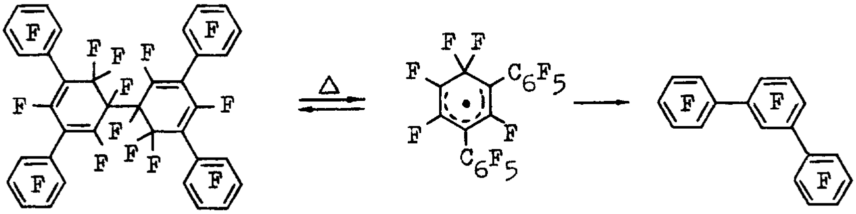
[b] See Ref. 7.

Attack at the orthoposition is hindered by the steric effect of the fluorine atoms both in DFD and in the attacking pentafluorophenyl radical since attack on diphenyl by the pentafluorophenyl radical (see Table 2) noticeably reduces the extent of orthosubstitution as compared to the reaction between diphenyl and the phenyl radical. The high reactivity of the metaposition in DFD has been mentioned above in discussing the scheme for the formation of perfluorotetrakis(phenyl)tetrahydrodiphenyls. Although the factors which determine such unusual reactivity at the metaposition in DFD are not particularly clear, it should be noted that the ratio of the sum of the yields of o- and p-terphenyls to the yield of the m-isomer is lower in the reaction between diphenyl and the pentafluorophenyl radical than in the reaction between diphenyl and the phenyl radical. The unexpected reactivity of the metaposition in DFD seems to depend not only on the effect of the fluorine atoms in DFD but also on the nature of the attacking radical.

The ratios of the isomeric perfluoroterphenyls (m > p > o) probably depend on the relative reactivities of the various positions in DFD since it is known that in phenylcyclohexadienyl radicals neither isomerization with phenyl migration nor fragmentation with phenyl radical formation occurs [8]. The study of the thermolysis of dimers (I) and (IV) in benzene solution shows that the addition of the pentafluorophenyl radical to polyfluoroaromatic compounds is irreversible. Dimers (I) and (IV) did not decompose at 200°C (for 20 hours) but at 250°C they yielded DFD and m-perfluoroterphenyl, respectively.



(I)



(IV)

Stabilization of the σ-complexes formed during thermolysis appear to occur by removal of fluorine atoms at the walls of the reaction vessel, but a secondary disproportionation giving rise to substituted perfluorocyclohexadienes as well as DFD and m-perfluoroterphenyl cannot be ruled out. The IR spectra of the mixture of resinous products obtained by thermolysis reveal the presence of an absorption corresponding to the vibrations of the fluorinated double bond, in addition to absorption bands corresponding to the vibrations of the C—F bond and the fluorinated aromatic ring.

EXPERIMENTAL

IR spectra were recorded on a UR-20 instrument with an NaCl window employing KBr discs. UV spectra were recorded using ethanol solutions in a Specord instrument. The ^{19}F NMR spectra were obtained with a Varian A56/60$_A$ spectrometer operating at 56.4 MHz. Hexafluorobenzene was used as an external reference. GLC analyses were performed on a LHM-7a Gas Chromatograph using 4m x 4 mm stainless steel columns packed with 15% SKTFT on Chromosorb W.

The reaction of pentafluorobenzoyl peroxide with decafluorodiphenyl

Decafluorodiphenyl (22.3 g) and pentafluorobenzoyl peroxide (7.0 g) were heated in a sealed tubes for 40 h at 80°C. The reaction mixture (26.4 g) was treated with hexane and undissolved perfluoro-3,3',5,5'-tetrakisphenyl-1,1'2,2'-tetrahydrodiphenyl-1,1'(nc), (0.6 g) was filtered off; m.p.229-230°C (from CCl_4). IR spectrum, cm^{-1}: 660m, 740w, 980s, 1000s; 1040-1070s (C - F); 1500 - 1530s (C_6F_5); 1740w (-CF=CF-). UV spectrum, nm: λ_{max} 221 (log ε 4.27), 224 (shoulder) (log ε 4.04), 265 (shoulder) (log ε 3.86). Found (%): C 43.12, 42.83; F 56.84, 56.93; Mol.wt. 1007, 1008 (isothermic distillation). $C_{36}F_{30}$ requires (%): C 43.12, F 56.88; Mol.wt. 1002. The hexane solution was passed through a 1.2m x 40 mm column filled with silica gel. Elution with hexane yielded unreacted DFD and isomeric perfluoroterphenyls (15.4 g). GLC analysis showed this mixture to contain 1.9% perfluoro-p-terphenyl, 3.9% perfluoro-m-terphenyl and 0.6% perfluoro-o-terphenyl (nc). By preparative-scale GLC from this mixture the following were isolated: perfluoro-p-terphenyl, m.p.192.5-193.5°C (191.5-193.5°C [9]); perfluoro-m-terphenyl, m.p.126-127°C (125-126°C [9]); perfluoro-o-terphenyl, m.p.114.5-115°C. The ^{19}F NMR spectrum (25% CCl_4 solution) exhibited signals at -2.3, -12.5 -23.5, -27.4 ppm in an intensity ratio of 2:2:2:1, respectively. IR spectrum (cm^{-1}): 720s, 750s, 970m, 1000s, 1060s, 1100s (F-C); 1490-1520s, 1640m (C_6F_5). UV spectrum (nm): λ_{max} 222 (log ε 4.32), 240(shoulder) (log ε 4.04), 270 (log ε 3.60). Found (%): C 45.05 45.07; F 55.26, 55.00; Mol.wt. 498, 501 (isothermic distillation). $C_{18}F_{14}$ requires (%): C 44.82, F 55.18; Mol.wt. 482. Elution with CCl_4 yielded 9.4 g of a yellowish product, m.p. 85-100°C. IR spectrum (cm^{-1}): 740m, 820w, 1000s, 1040-1070s (C–F); 1500-1530s (C_6F_5); 1710w, 1740w, 1770w (-CF=CF-). The ^{19}F NMR spectrum (20% CCl_4 solution) exhibited signals relative to C_6F_6 at 3.5, -2.3, -14.2, -22.4 ppm in an intensity ratio of 1:4:2:4, respectively, and three broadened signals at -54.1, -60.2 and -69.8 ppm with a total intensity of 4. Found (%): C 42.70, 43.00; F 55.91, 56.14. $C_{36}F_{30}$ requires (%): C 43.12, F 56.88.

The defluorination of perfluoro-3,3',5,5'-tetrakis(phenyl)-1,1', 2,2'-tetrahydrodiphenyl-1,1' (IV)

A mixture consisting of 0.50 g (IV) and 5.00 g of zinc dust in 10 cm^3 of glacial acetic acid was stirred for 4 h at 120°C. The zinc dust was filtered off and the filtrate diluted with cold water to precipitate perfluoro-3,3',5,5'-tetrakis(phenyl) diphenyl-1,1' (nc); weight 0.47 g (97.5%), m.p.199-201°C (sublimation). IR spectrum (cm^{-1}): 680m, 1000s, 1080s (C–F); 1420m, 1480s, 1505s, 1525s, (C_6F_5). UV spectrum (nm): λ_{max} 231 (log ε 2.38), 272 (log ε 1.82). Found (%): C 46.95, 46.66, F 53.27, 53.08; Mol.wt. 926 (mass spectrum). $C_{36}F_{26}$ requires (%): C 46.65, F 53.35; Mol.wt. 926.

The defluorination of isomeric perfluorotetrakis(phenyl)tetrahydrodiphenyls

The isomeric perfluorotetrakis(phenyl)tetrahydrodiphenyls (5.0 g) and 25.0 g of zinc dust in 50.0 cm^3 glacial acetic acid were stirred for 6 h at 120°C. The zinc dust was filtered off and washed with hot acetic acid. The combined filtrates were poured into cold water, and the white precipitate formed was filtered to obtain 4.5 g (96%) of product; m.p.80-100°C. Found (%): C 46.60, 46.73, F 53.22, 52.99; Mol.wt. 926 (mass spectrum).

$C_{36}F_{26}$ requires (%): C 46.65, F 53.35; Mol.wt. 926.

The thermolysis of perfluoro-3,3'-bis(phenyl)-1,1',4,4'-tetrahydrodiphenyl-1,1' (I)

A solution consisting of 0.14 g of compound (I) in 0.4 cm^3 absolute C_6H_6 was heated in a sealed tube for 20 h at 250°C. After distillation of the solvent, the residue (0.14 g) was passed through a 250 mm x 20 mm column packed with silica gel. Elution with hexane yielded 0.12 g of a yellowish product, m.p. 55-65°C. GLC analysis showed that this mixture contained 93% DFD and traces of pentafluorodiphenyl. Elution with acetone yielded 0.02 g of a brown resinous product.

The thermolysis of perfluoro-3,3',5,5'-tetrakis(phenyl)-1,1',2,2'-tetrahydrodiphenyl-1,1' (IV)

A mixture consisting of 0.20 g (IV) in 0.4 cm^3 absolute C_6H_6 was heated for 5 h at 250°C. GLC analysis showed this mixture contained 86% perfluoro-m-terphenyl.

The reaction of pentafluorobenzoyl peroxide with diphenyl

A mixture consisting of 1.5 g diphenyl and 1.1 g pentafluorobenzoyl peroxide was heated in a sealed tube for 5 h at 200°C. The ratios of isomeric terphenyls obtained (GLC data) are listed in Table 2.

REFERENCES

1 L.V. Vlasova, L.S. Kobrina and G.G. Yakobson, Zh. Organ. Khim., 10 (1974) 787.

2 L.V. Vlasova, L.S. Kobrina and G.G. Yakobson, Izv. Sib. Otdelenia AN SSSR, Ser. Khim. Nauk, No. 7 (3) (1974) 97.

3 L.V. Vlasova, L.S. Kobrina and G.G. Yakobson, Zh. Organ. Khim., 10 (1974) 792.

4 Yu.V. Pozdnyakovich, T.V. Chuikova and V.D. Steingartz, Zh. Organ. Khim., 11 (1975) 1689.

5 D. Callander, P.L. Coe and J.C. Tatlow, Tetrahedron, 22 (1966) 419.

6 H. Stangl and G. Juppe, Chem. Ber., 102 (1969) 2419.

7 J.M. Birchall, L.R. Evans and R.N. Haszeldine, J. Chem. Soc., Perkin 1, (1974) 1715.

8 D.J. Atkinson, M.J. Perkins and P. Ward, J. Chem. Soc., (C) (1971) 3240.

9 J. Thrower and M.A. White, Amer. Chem. Soc., Div. Polymer Chem., Preprints, 7 (2) (1966) 1077.