ESR study of the 1,2-migration of F atoms in polyfluorinated radicals

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The 1,2-migration of the F atom in polyfluorinated cyclohexadienyl radicals generated in the reaction of perfluoro-*p*-xylene with pentafluorobenzoyl peroxide has been observed directly by ESR.

Key words: pentafluorophenyl radical; polyfluorinated cyclohexadienyl radicals, fluorine 1,2-migration.

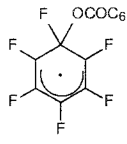
Previously,[1] rearrangement of intermediate polyfluorinated cyclohexadienyl radicals (CHDR) with migration of a F atom from the geminal position to a neighbouring position has been observed in a study of radical reactions of polyfluorinated compounds. This rearrangement is typical of CHDR containing the following substituents at the geminal position: Me, *cyclo*-C_6H_{11}, Ph, and C_6F_5. However, this rearrangement does not take place when C_6F_5COO or CF_3 groups are present. The occurrence of rearrangement is confirmed by the appearance of CF_2 groups in the products of radical reactions involving perfluoroarenes, *viz.*, CHDR dimers.

In a continuation of the study of radical reactions of perfluoroaromatic compounds, we attempted to observe directly the rearrangement of CHDR by detecting polyfluorinated CHDR by ESR. This method has been successfully used previously[2,3] for characterizing CHDR formed in reactions of hexafluorobenzene with photolysis-generated radicals. In the present work, we generated radicals by the thermal method.

When a solution of pentafluorobenzoyl peroxide in hexafluorobenzene was heated (80 °C) or decomposed photochemically (~20 °C), the ESR spectrum of a radical was recorded. Based on an analysis of the coupling constants (Table 1), we ascribed the structure of perfluoro-1-benzoylcyclohexadienyl radical (**1**) to this species. The value of $a_{F(1)}$ in the spectrum of radical **1**, which is the most sensitive to the nature of the substituent at the geminal position, is close to that for polyfluorinated CHDR containing substituted benzoyloxy groups (4-$ClC_6H_4C(O)O$: $a_{F(1)}$ = 88.0 G; 4-$MeOC_6H_4C(O)O$: $a_{F(1)}$ = 89.4 G at 25 °C).[3] The other coupling constants of radical **1** (see Table 1) are also similar to the corresponding parameters for polyfluorinated CHDR. The small differences between the coupling constants of the samples of **1** generated by the thermal and photochemical methods probably appear because these parameters depend on temperature.

Similarly, during the photochemical decomposition of *p*-fluorobenzoyl peroxide in hexafluorobenzene (~20 °C) we managed to detect, as the main product, a spin-adduct of the *p*-fluorobenzoyl radical with hexafluorobenzene (**2**) (see Table 1). Probably, the relatively high stability of the pentafluorobenzoyloxyl and *p*-fluorobenzoyloxyl radicals under the conditions of

Table 1. Coupling constants (*a*/G) for polyfluorinated cyclohexadienyl radicals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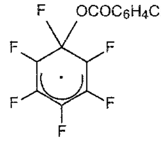
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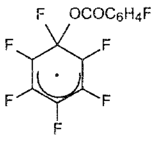
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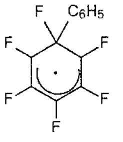
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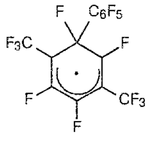
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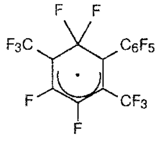
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a	**1a**	**1**	**2**	**2a**	**3**	**4**
$a_{F(1)}$	88.0[a]	82.0 (83.2)[b]	~84.8	107.3[c]	69.2	50.4, 50.0
$a_{F(2,6)}$	23.0	22.4 (22.4)	~21.1	23.0	18.0	—
$a_{F(3,5)}$	6.7	6.5 (6.8)	~6.8	6.5	9.6	6.5
$a_{F(4)}$	37.0	36.8 (36.6)	~36.0	37.4	48.0	38.2
$a_{2\text{-}CF_3}$	—	—	—	—	18.0, 2.0	14.4, 2.1, 2.1
$a_{6\text{-}C_6F_5}$	—	—	—	—	—	6.5, 2.1, 2.1

[a] Literature data.[3] [b] The numbers in parentheses indicate the coupling constants for radical **1** generated photochemically at 25 °C. [c] Literature data.[2]

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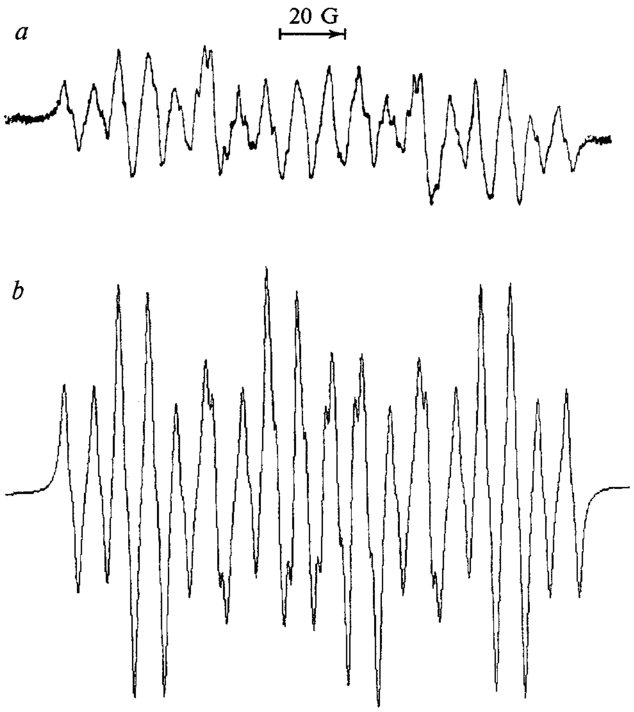


Fig. 1. ESR spectrum of radical **3** at 90 °C: *a*, experimental; *b*, calculated.

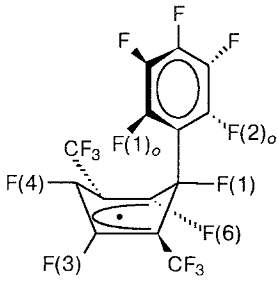
their thermal and photochemical generation (*cf.* the increase in stability of the benzoyloxyl radicals due to the introduction of substituents into the aromatic ring[3]) was responsible for the fact that we were unable to observe a spin-adduct of the pentafluorophenyl radical with hexafluorobenzene. In the case of the *p*-fluorophenyl radical, only a minor amount of such an adduct was formed. The data obtained are consistent with our observations that the main direction of the reaction between pentafluorobenzoyl peroxide and hexafluorobenzene at 80 °C is the addition of the pentafluorobenzoyloxyl radical to hexafluorobenzene.[4,5]

Since thermal decomposition of pentafluorobenzoyl peroxide in hexafluorobenzene yields the corresponding dimers, we used perfluoro-*p*-xylene, which makes it possible to generate radicals from peroxides at higher temperatures, as the substrate.

When pentafluorobenzoyl peroxide is heated (90—100 °C) in perfluoro-*p*-xylene, the ESR spectrum of the cyclohexadienyl radical **3** is recorded (see Table 1, Fig. 1). This agrees with the data obtained previously[6] for the decomposition of pentafluorobenzoyl peroxide in octafluorotoluene at 80—200 °C, which indicate that only the pentafluorophenyl radical participates in the reaction. The $a_{F(1)}$ value for radical **3** is less than the corresponding coupling constants both for polyfluorinated benzoyloxy-CHDR and aryl-CHDR.[2,3] The low value of the $a_{F(1)}$ constant probably results not only from the strong electron-withdrawing ability of the pentafluorophenyl group at the geminal position of radical **3** but also from the considerable steric interaction between the geminal position and the CF_3 group at position 2 of the cyclohexadienyl ring. This interaction probably results in withdrawal of the geminal position from the plane and distortion of the plane of the π-system of the cyclohexadienyl moiety. Probably, it is the latter effect that makes the $a_{F(3)}$, $a_{F(4)}$, and $a_{F(6)}$ values for radical **3** differ from those typical of coupling constants for unsubstituted polyfluorinated CHDR (see Table 1).[2,3]

A nonplanar structure of CHDR has already been postulated both for hydrogen-containing radicals[7] and those that are polyfluorinated.[2] For example, the nonplanarity of the cyclohexadienyl radical was used as an explanation for the decrease in the splitting constant of the geminal F atom of fluorinated CHDR formed by the addition of primary, secondary, and tertiary radicals to hexafluorobenzene.[2] However, it should be noted that the degree of distortion of the π system of the cyclohexadienyl radical has not been considered (*cf.* the data of quantum chemical calculations[8]).

The ESR spectrum of radical **3** contains additional coupling constants, 18.0 and 2.0 G, which we assigned to splitting on the F atoms of the CF_3 group at position 2 of the cyclohexadienyl ring ($a_{2\text{-}CF_3}$).



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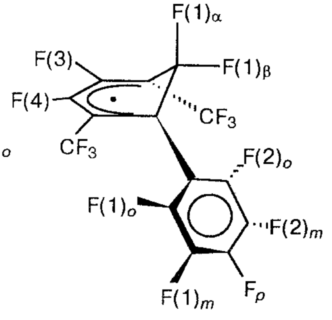

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When the temperature of the reaction between pentafluorobenzoyl peroxide with perfluoro-*p*-xylene is increased to 120—138 °C, the ESR spectrum displays noticeable changes that suggest the formation of a new radical, **4** (Fig. 2). The value of $g = 2.0037 \pm 0.0003$ obtained for CHDR **4** is typical of radicals of this class.[2] The spectrum contains two similar coupling constants $a_{F(1)}$, which indicates isomerization of radical **3** with migration of the F atom from the geminal position to the neighboring carbon atom of the CF group. Hence, radical **4** has the structure of perfluoro-2,5-dimethyl-6-phenylcyclohexadienyl. The $a_{F(1)}$ coupling constant for radical **4** is much lower than that in the case of polyfluorinated CHDR with CFR in the geminal position (see Table 1), which is in agreement with the well-known fact that the $a_{F(1)}$ value depends on the steric interactions of the substituent at the geminal position and on its electronegativity.[2] For example, if alkoxyl substituents that have small volumes but high electronegativity are present, the value of $a_{F(1)}$ for

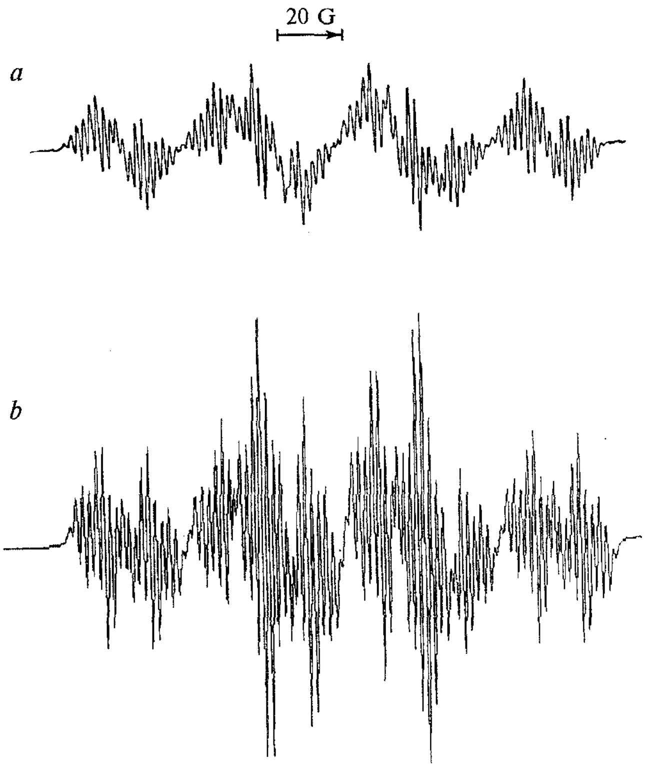


Fig. 2. ESR spectrum of radical **4** at 130 °C: *a*, experimental; *b*, calculated.

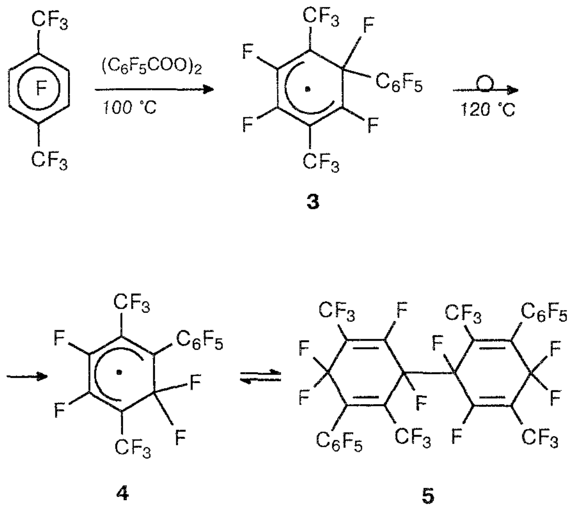
polyfluorinated CHDR is lower than the corresponding constant for aryl and alkyl substituents, and reaches 65—69 G; an even lower $a_{F(1)}$ value has been predicted for CF_2 in the geminal position.

Two $a_{F(1)}$ constants, 50.0 and 50.4 G, are observed in the spectrum of radical **4**, in which CF_2 is in the geminal position. The presence of two coupling constants implies that the F atoms at the geminal position are nonequivalent, which may be because the position is outside the molecule plane. However, the similarity of these constants suggests that the distortion is insignificant and does not affect the planarity of the cyclohexadienyl moiety in radical **4**. Unlike in its precursor, radical **3**, the coupling constants of the F atoms of the cyclohexadienyl moiety in radical **4** ($a_{F(4)}$ = 38.2 G and $a_{F(3)}$ = 6.5 G) are similar to those of the hexafluorocyclohexadienyl radicals substituted only at the geminal position (34—38 and 5—7 G, respectively).[2] This is probably related to a decrease in the steric interactions that distort the π-system plane in radical **3**.

In addition to the above coupling constants in the ESR spectrum of radical **4**, six more coupling constants are observed: the constant at a = 6.5 G corresponds to splitting on the F_p atom, while two coupling constants at a = 2.1 G refer to splitting on the F_o atom of the pentafluorophenyl ring. The constants at a = 14.4 G and two constants at a = 2.1 G were attributed to splitting on the CF_3 group at position 2 of the cyclohexadienyl ring. The nonequivalence of the F atoms of this CF_3 group in radicals **3** and **4** is likely to be caused by steric factors.

It should be noted that radicals **3** and **4** do not display coupling constants with the fluorine atoms of the CF_3 group at position 5 of the cyclohexadienyl moiety. We believe that this is consistent with the low spin density in positions 3 and 5 of CHDR.

The structure of radical **4** is additionally supported by the fact that this radical is generated by heating (100—130 °C) dimer **5**, which we isolated preparatively from the products of decomposition of pentafluorobenzoyl peroxide in perfluoro-*p*-xylene at 140 °C.



Heating pentafluorobenzoyl peroxide in perfluoro-*p*-xylene at 120—130 °C produces not only radical **4** but also one more radical. The ESR spectrum of the latter can be observed after cooling the system to ~20 °C, when radical **4** is removed from the system due to the formation of dimer **5**. It is difficult to reveal the structure of this radical since the signals in its spectrum have an unresolved structure. However, we can assume that this radical is formed due to the second possible direction of migration of the F atom in radical **3**, namely, from the geminal position to the adjacent position containing a CF_3 substituent. This assumption is based on the absence of migration of the F atom in CHDR formed in reactions of hexafluorobenzene and decafluorobiphenyl with sources of perfluoroalkyl radicals.[3,10]

Experimental

ESR spectra were recorded on an ESR-221 instrument equipped with a high-temperature unit and a system for the photochemical generation of radicals. The concentration of the solutions used to record the ESR spectra was 6—10 %. The ^{19}F NMR spectrum was recorded on a Bruker AC 200 spectrometer using C_6F_6 as the internal standard. The mass spectrum (EI, 70 eV) was recorded on a Finnigan MAT-8200 GC/MS mass spectrometer.

Perfluoro-2,2′,5,5′-tetramethyl-3,3′-diphenyl-1,1′,4,4′-tetrahydro-1,1′-diphenyl (5). A mixture of pentafluorobenzoyl peroxide (2.0 g) and perfluoro-*p*-xylene (20.0 g) was refluxed for 4 h at 170 °C and then cooled. The excess perfluoro-*p*-xylene was distilled off *in vacuo* (50—100 Torr). The residue (3.23 g) was chromatographed on a column with SiO_2 (using hexane as the eluent) to give 1.65 g of a white crystalline product, which predominantly consisted of compound **5** (^{19}F NMR spectroscopic data). Crystallization of the residue from hexane gave 0.96 g of compound **5**, m.p. 149—153 °C. ^{19}F NMR (10 % solution in $CDCl_3$), δ: −3.51 (F(1)); 2.23 (F_m); 14.89 (F_p); 26.09, 28.20 (F_o); 65.29 (F(6)); 69.36, 70.82 (F(4), AB-system, $J_{F,F}{}^{gem}$ = 330 Hz); 104.79 (C(2)—CF_3); 106.34 (C(5)—CF_3). The distinguishing feature of the ^{19}F NMR spectrum of dimer **5** is the presence of two signals of the F_o atoms due to hindered rotation of the pentafluorophenyl ring around the C—C bond. The signals were assigned by comparison with the corresponding chemical shifts for perfluoro-3,3′-diphenyl-5,5′-dimethyl-1,1′,4,4′-tetrahydro-1,1′-diphenyl.[6] MS, *m/z*: 906 $[M]^+$, 452.9761 $[M/2]^+$. Calculated for $C_{14}F_{15}$, *m/z*: 906 $[M]^+$, 452.9760 $[M/2]^+$.

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