

Perfluoropropylation of Aromatic Compounds with Bis(heptafluorobutyl) Peroxide

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Bis(heptafluorobutyl) peroxide could be used as a reagent for perfluoropropylation of aromatic compounds under mild conditions.

Owing to the high electronegativity of the perfluoroalkyl group, reactions involving a perfluoroalkyl cation as an intermediate are very limited. An exception is Umemoto's recent work, which reported the perfluoroalkylation of aromatic compounds using Rf⁺-carrier reagents, *e.g.* perfluoroalkylphenyliodonium trifluoromethanesulphonate.¹ Therefore, perfluoroalkylation *via* radical reactions should play an important role in synthetic chemistry. Perfluoroalkyl iodides have been used as radical sources for perfluoroalkyl groups (Rf•),² but this requires photoirradiation or high temperature whereas mild conditions are essential if free radical perfluoroalkylation is to be a synthetically useful tool. Bis(heptafluorobutyl) peroxide (**1**) is known to

decompose homolytically at 15–45 °C to give the heptafluoropropyl radical.³ In this paper we report the perfluoroalkylation of an aromatic ring with (**1**), equation (1).

Peroxide (**1**) was prepared from heptafluorobutyl chloride and hydrogen peroxide in 1,1,2-trichloro-1,2,2-trifluoroethane (Freon-113) according to the literature.³ The solution of (**1**) in Freon-113 was used without further purification and the concentration of the peroxide was determined by iodometry.

The thermal decomposition of (**1**) in the presence of anisole, toluene, benzene, chlorobenzene, and nitrobenzene under degassed conditions was studied. The rates, the activation parameters, and the products of the decomposition of (**1**) are


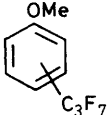
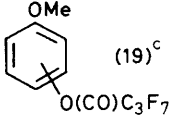

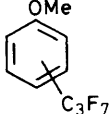
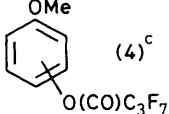
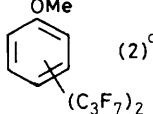

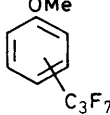
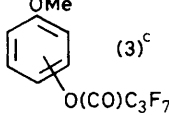
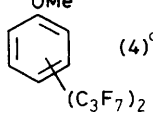
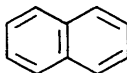
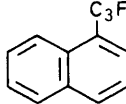
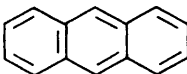
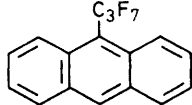

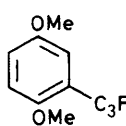
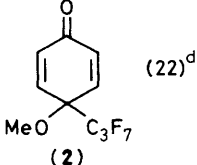
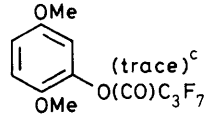
Table 1. Thermal decomposition of (**1**) in Freon-113 in the presence of benzenes.

Substrate	ΔH^\ddagger (kcal mol ⁻¹) ^a	ΔS^\ddagger (e.u.) ^a	$k_d \times 10^5$ (s ⁻¹) ^b (at 15 °C)	Yield of ArC ₃ F ₇ (%)	Yield of C ₃ F ₇ CO ₂ H (%)	Total rate ratio (k_X/k_H) ^c
PhOMe	19.69 ± 0.64	-8.54 ± 2.22	9.03 ± 0.26	93 (1:0.55:1.87) ^e	82	2.85 ^d
PhMe	15.06 ± 1.00	-24.41 ± 1.72	9.94 ± 0.33	85 ^f	77	2.80
PhH	21.14 ± 0.95	-5.21 ± 3.28	4.15 ± 0.09	86	78	—
PhCl	23.51 ± 1.04	1.31 ± 3.60	1.74 ± 0.04	45 (1:0.09:1.99) ^e	54	0.27 ^d
PhNO ₂	22.33 ± 1.07	-4.06 ± 3.62	0.91 ± 0.08	trace		
None	24.07 ± 1.81	1.81 ± 0.08	0.78 ± 0.01			

^a 1 kcal = 4.184 kJ. 1 e.u. = 1.986 cal K⁻¹ mol⁻¹. ^b 0.02 mol dm⁻³ (**1**), 0.10 mol dm⁻³ benzenes in Freon-113. ^c From the relative yields of heptafluoropropyl benzenes obtained from benzene and chlorobenzene, toluene, or anisole, total rate ratios were calculated.

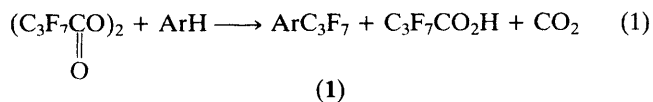
^d Partial rate factors were obtained from orientations: k_o/k = 2.57, k_m/k = 1.42, k_p/k = 9.66 in anisole, k_o/k = 0.263, k_m/k = 0.01, k_p/k = 1.05 in chlorobenzene. ^e These could possibly be the *ortho:meta:para* isomer ratios respectively if the i.r. aromatic C–H bend is diagnostic of structure: C₃F₇C₆H₄OMe: *o*; 750 cm⁻¹, *m*; 823, 785, 705 cm⁻¹; *p*; 835 cm⁻¹, C₃F₇C₆H₄Cl: *o*; 760 cm⁻¹, *p*; 828 cm⁻¹. The ratio was determined by g.c. ^f *o,m,p*-Isomers could not be separated by g.c.

Table 2. Perfluoropropylation of aromatic compounds with (1).

Substrate	Molar ratio substrate : (1)	Products (% yield)		
	2.0 ^a	 (47) ^c	 (19) ^c	
	2.0 ^b	 (93) ^c	 (4) ^c	 (2) ^c
	1.0 ^b	 (74) ^c	 (3) ^c	 (4) ^c
	1.8 ^b	 (61) ^d		
	2.0 ^b	 (49) ^d		
	1.2 ^b	 (33) ^d	 (22) ^d	 (trace) ^c

Conditions: ^a under air, ^b degassed. ^c Products were determined by g.c.-m.s. and the yields were determined by g.c. based on (1). ^d Isolated yields based on (1). Satisfactory spectral data were obtained for each product. α -Heptafluoropropyl naphthalene: n.m.r.; δ_C 124.2 (d), 126.3 (d), 127.5 (d), 127.7 (d, J_{CCF} 8.5 Hz), 127.8 (d), 128.9 (d), 133.3 (d), δ_F 1.43, 26.90, 46.48 p.p.m. (from CF_3CO_2H), i.r.; $\nu(CF_3)$ 1350, $\nu(CF_2)$ 1230, 1205 cm^{-1} , mass spectrum; 296 (M^+). 9-Heptafluoropropyl anthracene: n.m.r.; δ_C 124.9 (d), 126.4 (d), 127.8 (d), 129.3 (d), 134.2 (d), i.r.; $\nu(CF_3)$ 1350, $\nu(CF_2)$ 1220 cm^{-1} , mass spectrum; 346 (M^+), m.p.; 80–82°C (lit.¹ 84–87°C).

summarized in Table 1. The decomposition of (1) was accelerated by the addition of benzene, toluene, and anisole; perfluoroalkylated benzenes and heptafluorobutyric acid were obtained as the products in good yields. However, chlorobenzene and nitrobenzene did not accelerate the decomposition of (1) so much, and the yields of the heptafluoropropylbenzenes were low.



The activation entropy of the decomposition of (1) in the presence of benzenes suggests that the reaction proceeds bimolecularly. The total rate ratios for perfluoroalkylation with (1) obtained from the relative yields of heptafluoropropylbenzenes in chlorobenzene, toluene, and anisole to benzene indicate the character of the substitutions to be electrophilic. The partial rate factors are very different from those of the usual free radical aromatic substitutions,⁴ but similar to those for aromatic substitution by nitrobenzene-

sulphonyl peroxide.⁵ The high selectivity in the *p*-position indicates that the reaction proceeds by an orbital control mechanism.⁶ The reaction is probably started by the initial intermolecular interaction between the antibonding (σ^*) O–O bond of (1) and the π -electrons of the benzene.

The production of heptafluorobutyric acid ($C_3F_7CO_2H$), not heptafluoropropane (C_3F_7H), as a result of hydrogen abstraction should be important from synthetic viewpoints; the acid could be recovered as its sodium salt from the reaction mixture and used again for the preparation of the peroxide (1). In the decomposition of (1) in the presence of toluene, only a trace amount of 1,2-diphenylethane, which was a product from the coupling of benzyl radicals produced by hydrogen abstraction from toluene by $C_3F_7\cdot$, was detected; perfluoroalkylation of the aromatic ring took place in preference to hydrogen abstraction from the methyl group. This result is in marked contrast to the reaction of toluene with acetyl peroxide; heating a solution of acetyl peroxide in toluene gives xylenes in very small amounts in addition to 1,2-diphenylethane as the major product and other dimeric or polymeric materials.⁷ Thus, peroxide (1) should be a

good reagent for perfluoropropylation of electron-rich benzene.

The reaction of anisole and (1) was examined under various conditions (Table 2). Perfluoroalkylation of electron-deficient benzene is slow, so the yields of di- or tri-fluoroalkylated benzenes should be low. In the reaction of an equimolar amount of anisole with (1), the yield of difluoroalkylated anisole was only 4%. When the reaction was carried out in air, considerable amounts of (heptafluorobutyryl)oxyanisoles were obtained in addition to the heptafluoropropylanisoles. So the perfluoroalkylation should be carried out under degassed conditions.

The perfluoropropylations of naphthalene, anthracene, or 1,4-dimethoxybenzene using (1) were also examined. To the solution of naphthalene, anthracene, or 1,4-dimethoxybenzene in Freon-113 or CCl₄ was added the solution of (1) in Freon-113, and the solution was allowed to stand at room temperature or at 0 °C, under degassed conditions until the peroxide was completely decomposed. The products were separated by column chromatography. The results are summarized in Table 2. α -Heptafluoropropyl naphthalene and 9-heptafluoropropyl anthracene were obtained as sole products with naphthalene and anthracene respectively. The reaction of (1) and 1,4-dimethoxybenzene was rapid even at 0 °C and gave the unexpected compound (2) in addition to

the substituted compounds. Zaho *et al.*⁸ reported that the reaction of (1) and 1,4-dimethoxybenzene gave mainly 2-[(perfluorobutyryl)oxy]-1,4-dimethoxybenzene. However, we could detect only trace amounts of ester-type products even after repeated experiments.

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References

- 1 T. Umemoto, Y. Kuriu, and H. Shuyama, *Chem. Lett.*, 1981, 1663.
- 2 J. M. Birchall, G. P. Irvin, and R. A. Boyson, *J. Chem. Soc., Perkin Trans. 2*, 1975, 435; Y. Kobayashi, I. Kumadaki, A. Ohsawa, S. Murakami, and T. Nakano, *Chem. Pharm. Bull.*, 1978, **26**, 1247; A. B. Cowell and C. Tamborski, *J. Fluorine Chem.*, 1981, **17**, 345.
- 3 Z. Chengxue, Z. Renmo, P. Heqi, J. Xiangshan, Q. Yangling, W. Chengjiu, and J. Xikui, *J. Org. Chem.*, 1982, **47**, 2009.
- 4 M. J. Perkins, 'Free Radicals,' vol. II, ed. J. K. Kochi, Wiley-Interscience, New York, 1973, ch. 16.
- 5 R. L. Dannley and G. E. Corbett, *J. Org. Chem.*, 1966, **31**, 153.
- 6 G. Klopman, 'Chemical Reactivity and Reaction Paths,' ed. G. Klopman, Wiley-Interscience, New York, 1974, ch. 4.
- 7 E. L. Eliel, K. Rabindran, and S. H. Wilen, *J. Org. Chem.*, 1957, **22**, 859.
- 8 C. Zhao, G. M. El-Taliawi, and C. Walling, *J. Org. Chem.*, 1983, **48**, 4908.