CONCLUSIONS

Reaction of stoichiometric quantities of perfluorocyclohexanone and 98% H_2O_2 in neutral media quantitatively forms α,α'-dihydroxydi(perfluorohexyl)peroxide, for which the main crystal and molecular structural parameters were determined by x-ray analysis.

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STERIC EFFECTS OF ORTHO SUBSTITUENTS IN REACTIONS OF PHENOLS AND PHENOLATES WITH POLYFLUOROKETONES

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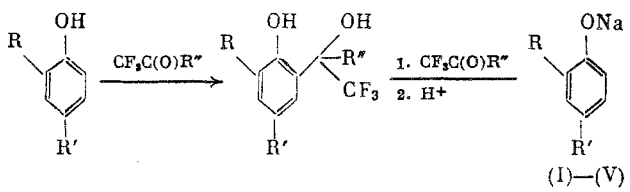
UDC 541.63:542.91:547.562:547.562.4'133:547.446.5'161

The uncatalyzed C-alkylation of *m*- and *p*-substituted phenols [1, 2] and phenolates [3-5] by polyfluoroketones (PFK) in nonpolar media proceeds regiospecifically at the *o*-position. It has been established [1] that in uncatalyzed C-alkylation at 25°C PFK react only with phenols, the m-substituents of which have a sufficiently high +M effect. It can be assumed that in this case the orientation is determined by the size of the substituent.

The present work is a study of the effect of the *o*-substituent on the conditions and direction of uncatalyzed C-alkylation of phenols and sodium phenolates in nonpolar media. In the course of the investigation it was found that in CCl_4 at 25°C, of the *o*-substituted carbo-



(I)—(V)

R = *t*-Bu, R′ = H, R″ = CF_3 (I); R = *t*-Bu, R′ = H, R″ = CF_2NO_2 (II); R = R′ = *t*-Bu, R″ = CF_3 (III); R = R′ = *t*-Bu, R″ = CF_2NO_2 (IV); R = CH_3, R′ = H, R″ = CF_3 (V).

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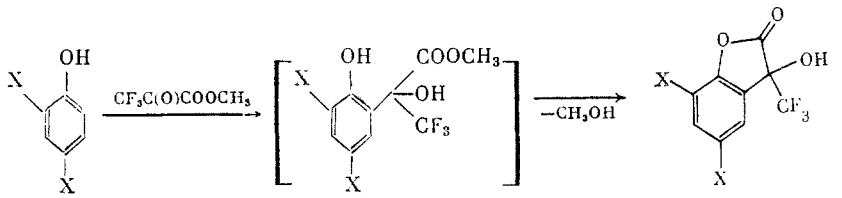
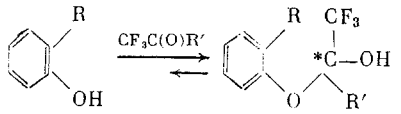
methoxy-, chloro-, bromo-, methyl-, tert-butyl-, methoxy-, and hydroxyphenols, only tert-butylphenol forms *o*-alkylation products (I) and (II) with hexafluoroacetone (HFA) and nitropentafluoroacetone (NPFA) (80% after 1 day, 100% after 2 days).

In the other cases no changes were observed after 15 days. The reaction of 2,4-di-tert-butylphenol with HFA, NPFA, and methyl trifluoropyruvate (MTFP) in CCl_4 at 20-25°C is finished within one day with quantitative formation of compounds (III), (IV), and (VI); in the case of MTFP the *o*-alkylation is accompanied by lactonization:



X = *t*-Bu. (VI)

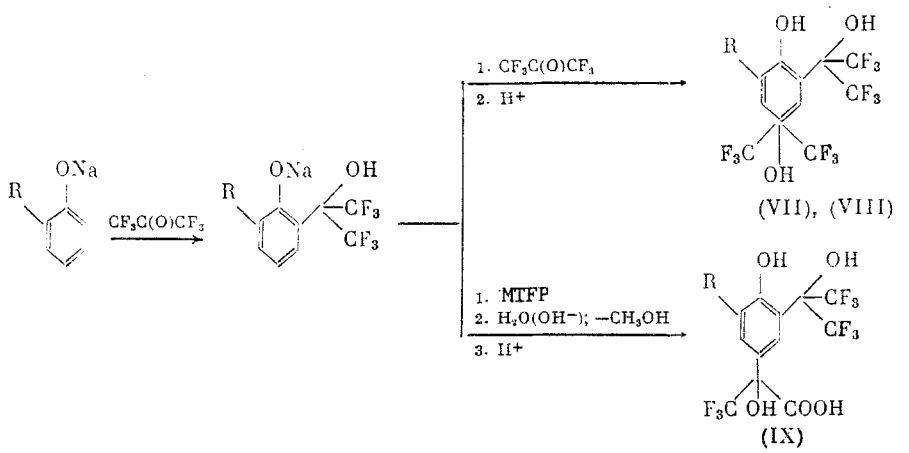
In the study of the reaction mixture it was observed that all of the phenols mentioned above that do not undergo C-alkylation by PFK at 25°C form O-alkylation products with MTFP and NPFA as soon as the reagents are mixed:



R = CH_3, OCH_3, Cl, Br, $COOCH_3$; R' = $COOCH_3$, CF_2NO_2, CF_3.

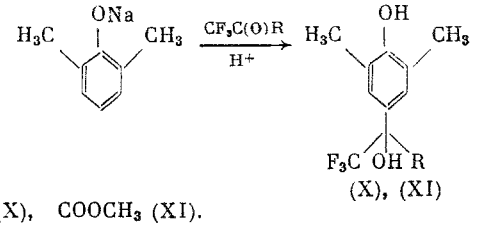
Evidence for this reaction is the appearance in the ^{13}C NMR spectrum of the typical signal of a similar polyketal with chemical shift in the 90-95 ppm region (corresponding to C* above) and the disappearance of the carbonyl signal of the ketones. The adducts that are formed decompose to the starting reagents when they are heated or when the solvent is removed. Analogous results were obtained in the reactions of *o*-phenols with HFA. At the same time in a ^{13}C and ^{19}F NMR study of the reaction mixture of *o*-tert-butylphenol and NPFA the typical signals for the O-alkylation product were not found; the ^{19}F NMR spectrum taken 0.5 h after the reagents were mixed shows two multiplets, at −4.40 and +13.40 ppm (3:2), corresponding to the A_2K_3 system NPFA.* In the IR spectra taken at 1 h intervals, the gradual decrease of the NPFA keto absorption band in the 1800 cm^{-1} region clearly correlates (according to TLC) with the accumulation of C-alkylation products. Apparently the absence in this case of the O-alkylation product can be attributed to steric hindrance created by the bulky tert-butyl and perfluoroalkyl groups; this agrees with the data of review [6]. Consequently the ability of *o*-tert-butylphenols to undergo C-alkylation by PFK at 25°C is evidently related to the absence of competing O-alkylation. In avoiding assumptions about any other specific effect of the tert-butyl group in the aromatic nucleus on this reaction it was shown that *p*-tert-butylphenol forms with PFK at 25°C only the O-alkylation product. Our results enable us to assume that in the case of phenols that tend to undergo O-alkylation, their C-alkylation by PFK is limited either by decomposition to the starting reagents or by rearrangement of the O-alkylation product. Thus the product of C-alkylation of *o*-cresol by HFA (V) is formed only upon heating above 100°C. However such phenols can easily be made to react in C-alkylation with PFK when they are in the form of sodium phenolates in Freon-113 by the previously proposed procedure [3-5]. Depending on the proportions of reagents, sodium *o*-cresolate forms with HFA either *o*-(V) or the product of *o,p*-dialkylation (VII). In the same way *o*-tert-butylphenolate reacts with HFA to form the respective compounds (I) and (VIII):

*The signals in the ^{19}F NMR spectra of the O- and C-alkylation products correspond to an ABK_3 system (see Experimental).



R = CH_3 (VII), (IX), *t*-Bu (XIII).

Treatment of *o*-cresolate in Freon-113 first with an equimolar amount of HFA, then with MTFP, followed by saponification with aqueous alkali gives acid (IX) in 71% yield. Sodium 2,6-xylenolate in Freon-113 with the same ketones (at 80°C for 0.5 h) easily forms the *p*-alkylation products (X) and (XI) in quantitative yield.



R = CF_3 (X), $COOCH_3$ (XI).

Starting from the existing data we can conclude that first of all the uncatalyzed reactions of *o*-substituted phenols and phenolates with PFK in nonpolar medium, regardless of substituent bulk, form *o*-alkylation products. Evidently the determining influence on orientation in these conversions is the participation of the OH and ONa groups in the formation of the transition states [5]. Secondly, as the bulk of the *o*-substitutent increases, O-alkylation of the phenols by PFK is hindered and C-alkylation is facilitated.

It can be assumed that phenols that do not contain an electron acceptor group in the nucleus, but have a bulky substituent in the *o*-position that hinders O-alkylation, can also be easily involved in C-alkylation by PFK.

TABLE 1. Properties of Compounds (I)-(IV), (VI)-(IX), and (XI)

Compound	Yield, %	Mp, °C (solvent)	R_f (acetone–CCl_4)	Found/Calculated, %			Empirical formula
				C	H	F	
(I)	99.0	64–65 (pentane)	0.39 (1:6)	49.60 / 49.37	4.71 / 4.43	35.97 / 36.08	$C_{13}H_{14}F_6O_2$
(II)	99.1	– *	0.35 (1:6)	45.32 / 45.48	4.27 / 4.08	27.74 / 27.70	$C_{13}H_{14}NF_3O_4$
(III)	100.0	115–120 (hexane)	0.55 (1,6)	54.60 / 54.84	6.13 / 5.91	30.38 / 30.65	$C_{17}H_{22}F_6O_2$
(IV)	100.0	65–67 (pentane)	0.50 (1:6)	50.88 / 51.13	6.01 / 5.51	23.19 / 23.81	$C_{17}H_{22}NF_3O_4$
(VI)	97.0	90–92 (pentane)	0.55 (1:6)	61.80 / 61.82	6.40 / 6.36	17.20 / 17.27	$C_{17}H_{21}F_3O_3$
(VII)	94.7	91–92 (hexane)	0.32 (1:3)	34.91 / 35.46	1.70 / 1.82	51.91 / 51.82	$C_{13}H_8F_{12}O_3$
(VIII)	81.0	65–71 (pentane)	0.38 (1:3)	39.96 / 39.83	2.79 / 2.90	47.36 / 47.30	$C_{16}H_{14}F_{12}O_3$
(IX)	71.0	160–163 (benzene)	0.14 (1:3)	37.37 / 37.50	2.12 / 2.16	41.00 / 41.10	$C_{13}H_9F_3O_5$
(XI)	99.5	102–105 (CCl_4)	0.31 (1:3)	51.81 / 51.80	4.68 / 4.64	19.93 / 20.50	$C_{12}H_{13}F_3O_4$

*n_D^{20} 1.4680.

TABLE 2. ^1H and ^{19}F NMR Spectra* of Compounds (I)-(IV), (VI)-(IX), and (XI)

Compound	δ, ppm (J, Hz)					
	H^3	H^4	H^5	H^6	OH	^{19}F
(I)	7.30 d	6.80 t	7.20 d	–	7.95 s 5.20 s	−2.9 s
	(7.7)					
		(8.0)				
(II)	7.40 d.d	6.95 t	7.28 br s	–	7.60 s 6.23 s	– **
	(8.0)					
		(8.5)				
(III)	7.45 d	–	7.27 br s	–	7.80 s 5.75 s	−3.33 s
	(2.0)					
(IV)	7.25 br s	–	7.22 br s	–	7.40 br s 6.40 br s	–
(VI)	–	7.40 d	–	7.48 d	4.00 br s	−1.10 s
		(2.0)				
(VII)	7.50 br s	–	7.75 br s	–	9.60– 9.10 br s 7.65 br s	−2.22 s −2.00 s
(VIII)	7.70 br s	–	6.70 br s	–	8.61 br s 4.68 br s 3.30 br. s	−2.20 s −1.70 s
(IX)	7.93 br s	–	7.70 br s	–	–	−2.22 s −0.44 s
(XI)	7.33 s	–	7.33 s	–	–	−1.30 s

*^1H and ^{19}F NMR spectra of compounds (I)-(IV), (VI), (VIII), and (XI) were obtained in $CDCl_3$; the others in acetone-d_6.
**^{19}F NMR spectra (δ, ppm; J, Hz) (II): −4.30 m (CF_3, $J_{CF_3-CF_2}$ = 10.5), +13.40 m, +15.04 m (CF_2, J_{FA-FB} = 168.8); (IV): −4.50 m (CF_3, $J_{CF_3-CF_2}$ = 11.8), +12.00 m, 14.00 m (CF_2, J_{FA-FB} = 168.8).

EXPERIMENTAL

^{13}C, ^1H, and ^{19}F* NMR spectra of the synthesized compounds were obtained in acetone, acetone-d_6, and $CDCl_3$ with a Bruker R-200 SV spectrometer with working frequencies of 50.31, 200.13, and 188.30 MHz respectively. Chemical shifts were determined relative to TMS (^{13}C, ^1H internal standard) and CF_3COOH (^{19}F internal standard). IR spectra were obtained with an R-20 spectrometer in a CaF_2 cuvette of 0.007 cm layer thickness; R_f values are given for Silufol-254 sheets (Kavalier, Czechoslovak. SSR) in 1:3 and 1:6 acetone–CCl_4. Substances were identified in UV light. Properties of compounds are given in Table 1, spectral properties in Table 2.

2-(2-Hydroxyhexafluoroisopropyl)-6-tert-butylphenol (I). (a) In a glass ampul were placed 6 g of 2-tert-butylphenol and 20 ml of anhydrous CCl_4, 7 g of HFA was condensed at −78°C, and the ampul was sealed. It was held at 25°C for 48 h, then opened. The solvent was removed to yield 12.6 g of chromatographically pure compound (I) which crystallized when cooled.

(b) In a glass ampul were placed 6.88 g of finely powdered anhydrous sodium 2-tert-butylphenolate and 35 ml of Freon-113, 8.3 g of HFA was condensed in the ampul at −78°C, and the ampul was sealed. With periodic shaking it was heated at 80-95°C for 2 h, cooled, opened,

*^{19}F NMR spectra of compounds (I), (III), (VII), and (IX) were obtained with a Perkin–Elmer R-32 spectrometer at 84.6 MHz working frequency.

and treated with excess dilute HCl. The organic layer was separated and dried over Na_2SO_4, and the solvent was removed to yield 13.5 g of oil, which crystallized when cooled. Recrystallization from pentane gave 12.0 g of (I).

2-(2-Hydroxy-1-nitropentafluoroisopropyl)-6-tert-butylphenol (II) was obtained from 0.75 g of 2-tert-butylphenol and 1.2 g of NPFA in 2.5 ml of CCl_4 kept for 48 h in a tightly closed flask. Removal of solvent gave 1.70 g of product (II) as a yellowish oil.

2-(2-Hydroxyhexafluoroisopropyl)-4,6-di-tert-butylphenol (III) was obtained by procedure (Ia) from 2.06 g of 2,4-di-tertbutylphenol and 2 g of HFA in 5 ml of CCl_4 after 24 h. Removal of solvent yielded 3.72 g of white crystalline (III).

2-(2-Hydroxy-1-nitropentafluoroisopropyl)-4,6-di-tert-butylphenol (IV) was obtained after r 24 h, analogously to the synthesis of (II) from 0.206 g of 2,4-di-tert-butylphenol and 0.2 g of NPFA in 0.5 ml of CCl_4. Substance (IV), 0.4 g, was obtained which crystallized on cooling.

2-(2-Hydroxyhexafluoroisopropyl)-6-methylphenol (V) was obtained analogously to (Ib) from 3.9 g sodium *o*-cresolate and 5 g of HFA in 20 ml of Freon-113 at 80° for 1 h. Substance (V), 7.9 g, was obtained. After recrystallization from hexane, its mp was 69-71°C.*

3-(Hydroxy-5,7-di-tert-butyl-3-trifluoromethyl-2(3H)-benzo[b]furanone (VI) was obtained analogously to (II) from 2.06 g of 2,4-di-tert-butylphenol and 2 g of MTFP in 5 ml of CCl_4 for 24 h. Removal of solvent yielded 3.2 g of substance (VI), which crystallized upon cooling.

2,4-Di(2-hydroxyhexafluoroisopropyl)-6-methylphenol (VII) was obtained by procedure (Ib) from 3.9 g of sodium *o*-cresolate and 11.60 g of HFA in 35 ml of Freon-113 at 85-95°C for 2 h. Dry product, 13.0 g, was obtained. Recrystallization from hexane yielded 12.5 g of white crystalline (VII).

2,4-Di(2-hydroxyhexafluoroisopropyl)-6-tert-butylphenol (VIII) was obtained by procedure (Ib) from 5.16 g of sodium 2-tert-butylphenolate and 11.6 g of HFA in 35 ml of Freon-113 at 85-95°C for 2 h as a yellowish oil that was crystallized from pentane. There was obtained 11.7 g of (VIII).

2-(2-Hydroxyhexafluoroisopropyl)-4-(2-hydroxy-2-carboxytrifluoroethyl)-6-methylphenol (IX) was obtained analogously by procedure (Ib), from 2.6 g of Na *o*-cresolate and 3.5 g HFA in 20 ml of Freon-113 at 80-85°C for 1 h as a white crystalline salt (IX). The ampul was cooled to −78°C and opened, and 3.5 g of MTFP in 15 ml of Freon-113 was added. Then the ampul was sealed, vigorously shaken, and heated to 20°C, then it was kept at 80°C for 0.5 h. After cooling to −78°C the ampul was opened, the solvent was removed, and the contents were treated with 50 ml of aqueous 20% KOH at 20°C for 3 days. The mixture was neutralized with conc. HCl to pH 1, and the resulting oil was extracted with ether (3 × 20 ml). The ether solution was dried over Na_2SO_4, the solvent was removed, and the residual oil was crystallized from benzene. There was obtained 5.67 g of (IX). ^{13}C NMR spectrum (δ, ppm; J, Hz): 167.63 (C=O), 155.23 (C^1), 129.88, 123.38 (C^3, C^5), 126.49, 124.01 (C^4, C^6), 122.53 (CF_3, J_{C-F} = 283.00), 121.87 (2 CF_3, J_{C-F} = 286.00 Hz), 79.17 ($C^*(CF_3)_2OH$, J_{C-CF^3} = 30.00), 76.46 (CF_3—C^*—COOH, J_{C-CF^3} = 29.00), 14.78 (CH_3).

4-(2-Hydroxyhexafluoroisopropyl)-2,6-dimethylphenol (X) was obtained analogously by procedure (Ia) from 4.32 g of Na 2,6-xylenolate and 6 g of HFA in 20 ml of Freon-113 at 80-85°C for 1 h. There was obtained 8.5 g of (X) as a white crystalline compound. Mp after recrystallization from hexane, 101-103°C (cf. [7]).

4-(2-Hydroxy-2-carbomethoxytrifluoroethyl)-2,6-dimethylphenol (XI) was obtained analogously by procedure (Ib) from 4.32 g of Na 2,6-xylenolate and 5.5 g of MTFP in 35 ml of Freon-113 at 80°C for 1 h. The ampul was cooled to −78°C and opened, and 20 ml of ether and 20 ml of 10% HCl were poured in. Then the ampul was shaken, and the organic layer was separated and dried over Na_2SO_4. Removal of solvent gave 8.3 g of chromatographically pure (XI).

CONCLUSIONS

1. In the reactions of phenols with polyfluorocarbonyl compounds, as the bulk of the *o*-substituent increases O-alkylation is hindered, so that C-alkylation is facilitated.

2. C-alkylation of *o*-substituted phenols and sodium phenolates by polyfluoroketones in nonpolar medium, regardless of substituent bulk, is regiospecific *o*-substitution; in the case of phenolates the subsequent *p*-alkylation also goes easily.

*Mp 67-72°C [7].

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SYNTHESIS OF FLUORO-CONTAINING SUBSTITUTED 1,3,5-TRIAZINES

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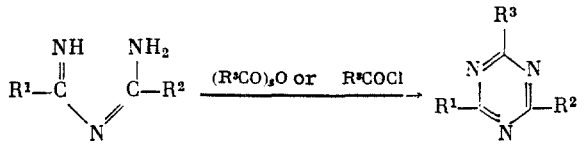
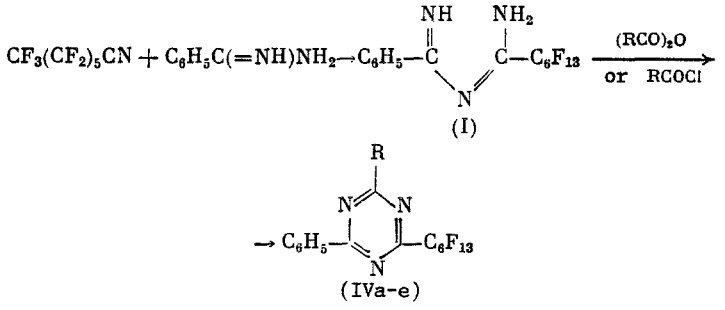
The synthesis and properties of triazines with identical substituents have been studied in detail: trisalkyltriazines [1, 2], trisperfluoroalkyltriazines [3, 4], and trisaryltriazines [1, 5]. The synthesis and properties of triazines with three different substituents have hardly been studied. Earlier, thermally stable 2-phenyl-4,6-perfluoroalkyl-1,3,5-triazines were prepared by cotrimerization of perfluoroalkanenitriles with benzonitrile [6] and also by reaction of the latter with tris-perfluoroalkyl-s-triazines [7].

For the synthesis of s-triazines with three different substituents R^1, R^2, and R^3, of which R^1 = phenyl and R^2 = perfluoroalkyl, the most useful method is acylation–cyclodehydration of N'-(perfluoroalkanimidoyl)benzamidines (imidoylamidines)* with anhydrides and acid halides of carboxylic acids because this makes it possible to prepare triazines with exactly determined positions of the substituents at the ring.



This article describes the synthesis of novel s-triazines by the method mentioned above. As starting compounds we used imidoylamidines (I) and (III), and bisimidoylamidine (II), prepared by reaction of mono- and dinitriles of perfluorocarboxylic acids with benzamidine. Subsequent cyclization of imidoylamidines (I)-(III) led to triazines (IV)-(VI).



*Imidoylamidines are also called 1,3,5-triaza-1,3-pentadienes with indication of the specific substituents at the 2 and 4 positions.

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