Perhalo Ketones. V.[1] The Reaction of Perhaloacetones with Aromatic Hydrocarbons

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Condensation of perhaloacetones (X_3CCOCX_3, X = F, Cl), with various aromatic hydrocarbons, and with their halogenated and alkylated derivatives, has led to the preparation of 28 new carbinols of the general structure $RC(CX_3)_2OH$. Using aluminum chloride as catalyst, yields decreased as the ketone used contained progressively more chlorine. The new compounds are chemically and thermally stable. An n.m.r. study of six of the compounds showed deshielding effects in adjacent aromatic or methyl protons resulting from the electron-withdrawing effect of an adjacent 2-hydroxyhexafluoro-2-propyl group.

Adjacent electron-withdrawing groups enhance the electrophilic character of the carbonyl carbon atom in perhalogenated ketones,[3] making possible the uncatalyzed reaction of hexafluoroacetone with aromatic amines[4,5] and phenols[6,7] to form the corresponding (2-hydroxyhexahalo-2-propyl)arene derivatives.

$$RC_6H_5 + X_3CCOCX_3 \longrightarrow RC_6H_4C(CX_3)_2OH$$
$$X = Cl, F$$

The present study is concerned with the preparation of similar materials from aromatic hydrocarbons, and their halogenated and alkylated derivatives, in reaction with hexafluoro- and with several fluorochloro-perhalogenated acetones. As confirmed in a report[7] which has appeared since initiation of this study, it has been found that aluminum chloride is an effective catalyst for this reaction. Carbinols of this type have previously been prepared only by the Grignard reaction.[3,4,7] Milder catalysts, such as toluenesulfonic acid or boron trifluoride, were found to be inoperative with the hydrocarbons, although they do facilitate reaction of the ketones with phenols[6] or with aromatic amines.[5] For example, no product was detected when a mixture of toluene, hexafluoroacetone, and toluenesulfonic acid was heated in an autoclave at 300° for 10 hr.

This procedure gives diminishing yields as the chlorine content of the ketone is increased. With hexafluoroacetone, reaction occurs rapidly and exothermally in the presence of a catalytic quantity of aluminum chloride to give good yields of the corresponding (2-hydroxyhexafluoro-2-propyl)arenes (*cf.* Table I). The low boiling point of hexafluoroacetone (−28°) has prompted the use of an autoclave for this reaction[7]; in the present study, satisfactory results were obtained at atmospheric pressure. Reaction occurs less easily with pentafluoromonochloroacetone and more than catalytic amounts of catalyst are required. In the case of *sym*-tetrafluorodichloroacetone, equivalent amounts of catalyst are required to achieve a good yield. Trifluorotrichloroacetone gave only mediocre yields (*cf.* Table II), together with large amounts of tarry materials, while *sym*-difluorotetrachloroacetone and hexachloroacetone did not give any isolable product. This decrease in activity of the ketone and increase in complexity of the reaction as fluorine is replaced by chlorine may be attributable to the concomitant decrease in the electrophilic character of the carbonyl carbon, greater steric hindrance of the bulky chlorine atoms, and the lower carbon–chlorine bond strength compared with carbon–fluorine.

TABLE I

PHYSICAL AND ANALYTICAL DATA OF (2-HYDROXYHEXAFLUORO-2-PROPYL)ARENES

Ar	B.p., °C. (mm.), or m.p., °C.	Yield, %	Calcd., % H	Calcd., % F	Found, % H	Found, % F
C_6H_5[a]	55–56 (12) 159–160 (760)	94	2.45	46.5	2.46	46.7
$4\text{-}CH_3C_6H_4$[b]	180–171 (760)	89	3.10	44.3	2.81	44.7
$2,4\text{-}(CH_3)_2C_6H_3$[b]	198–199 (760)	80	3.68	42.1	3.50	42.2
$3,4\text{-}(CH_3)_2C_6H_3$[b]	200–200.5 (760)	82	3.68	42.1	3.78	42.7
$2,5\text{-}(CH_3)_2C_6H_3$[b]	84–86 (20)	85	3.68	42.1	3.81	42.0
$4\text{-}ClC_6H_4$	189 (760)	76	1.79	40.8	1.60	40.6
$3(4)\text{-}Cl(CH_3)C_6H_3$	204 (760)	86	2.39	38.9	2.40	38.3
$2(4)\text{-}Cl(CH_3)C_6H_3$	210–211 (760)	68	2.39	38.9	2.33	38.5
$2(5)\text{-}CH_3(Cl)C_6H_3$	206–207 (760)	36	2.39	38.9	2.24	38.5
$2,3,5,6\text{-}(CH_3)_4C_6H$[c]	220–223 (760)	15	4.21	36.7	4.20	37.0
$4\text{-}C_{12}H_{25}C_6H_4$[c]	128–130 (2)	56	7.52	27.7	7.58	27.7
$4\text{-}C_6H_5C_6H_4$[c]	95	94	3.13	35.7	2.91	36.1
$4\text{-}C_6H_5CH_2C_6H_4$[c]	188–190 (16)	73	3.59	34.0	3.50	33.7
$1\text{-}C_{10}H_7$	134–135 (20)	89	2.72	38.8	2.85	39.7

[a] Known; ref. 3a and 7. [b] Orientation confirmed by n.m.r. [c] Orientation not proved experimentally; orientation of all other compounds established by alkaline cleavage.

In certain cases, the introduction of 2 equiv. of hexafluoroacetone per aromatic nucleus was found possible (Table III). The second 2-hydroxyhexafluoro-2-propyl group usually enters the ring primarily *meta* to the first one. A small yield of the *para* isomer, however, was also obtained from benzene, although others[7] observed formation of only the *meta* isomer. The two entering groups are oriented *meta* to each other in *o*- and *m*-xylene. However, in *p*-xylene, they are oriented *para* in the only product isolated (in 20% yield).

A previous[7] preparation of the bis product from benzene involved a two-step operation with intermediate isolation of the mono compound. In the present study, the bis material was prepared in one step, although introduction of the second fluoro ketone moiety required additional quantities of catalyst and a longer reaction time. Efforts to introduce three molecules of hexafluoroacetone were unsuccessful. At room tem-

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(1) Perhalo Ketones. IV: B. S. Farah and E. E. Gilbert, *J. Org. Chem.*, **30**, 1241 (1965). Papers V–VIII were presented at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964.

(2) To whom inquiries should be addressed.

(3) See, for example, (a) I. L. Knunyants, N. P. Gambaryan, C. Ching-Yun, and E. M. Rokhlin, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 684 (1962); *Chem. Abstr.*, **57**, 12305 (1963); (b) C. Woolf, Abstracts, 134th National Meeting of the American Chemical Society, New York, N. Y., Sept. 1957, p. 23M; (c) H. E. Simmons and D. W. Wiley, *J. Am. Chem. Soc.*, **82**, 2288 (1960).

(4) I. L. Knunyants, C. Ching-Yun, N. P. Gambaryan, and E. M. Rokhlin, *Zh. Vses. Khim. Obshchestva im. D. I. Mendeleeva*, **5**, 114 (1960); *Chem. Abstr.*, **54**, 20962 (1960).

(5) Perhalo Ketones. VI: E. E. Gilbert, E. S. Jones, and J. P. Sibilia, *J. Org. Chem.*, **30**, 1001 (1965).

(6) Perhalo Ketones. VII: B. S. Farah, E. E. Gilbert, M. Litt, J. A. Otto, and J. P. Sibilia, *ibid.*, **30**, 1003 (1965).

(7) D. C. England, French Patent 1,325,204 (1963); *Chem. Abstr.*, **59**, 11339 (1963).

TABLE II

PHYSICAL AND ANALYTICAL DATA OF (2-HYDROXYPERHALO-2-PROPYL)ARENES[a]

$Ar-C(CX_3)_2OH$	B.p., °C. (mm.), or m.p., °C.	Yield, %	Calcd., %			Found, %		
			Cl	F	H	Cl	F	H
$C_6H_5C(CF_2Cl)_2OH$[b]	98–100 (15)	70	25.63	27.4	2.17	25.42	27.4	2.12
$4-ClC_6H_4C(CF_2Cl)_2OH$	124–125 (20)	56	22.8	24.6		22.8	24.4	
$4-CH_3C_6H_4C(CF_2Cl)_2OH$	115–116 (14)	58	24.40	26.12	2.75	24.16	26.3	2.71
$2,5-(CH_3)_2C_6H_3C(CF_2Cl)_2OH$	94–95 (2)	34	23.24	24.9	3.28		24.5	3.43
$3,4-(CH_3)_2C_6H_3C(CF_2Cl)_2OH$	129–130 (15)	64	23.24	24.9	3.28	23.65	24.5	3.41
$2(5)-CH_3(Cl)C_6H_3C(CF_2Cl)_2OH$	182–184 (2)	7	23.24	24.9	3.28	23.41	24.7	3.30
$3,4-(CH_3)_2C_6H_3C(CF_2Cl)(CFCl_2)OH$	148 (4)	12	33.16	17.3		33.05	17.1	
$4-C_6H_5C_6H_4C(CF_2Cl)_2OH$	71–72	68	20.23	21.6	2.82	20.63	21.8	2.50

[a] Orientation of entering group not established experimentally. [b] Known; ref. 7.

TABLE III

PHYSICAL AND ANALYTICAL DATA OF SOME BIS(2-HYDROXYHEXAFLUORO-2-PROPYL)ARENES

Compd. [$R = C(CF_3)_2OH$]	B.p., °C. (mm.), or m.p., °C.	Yield, %	Calcd., %		Found, %	
			F	H	F	H
$1,3-R_2C_6H_4$[a,b]	209 (760); 99 (20)	84	55.5	1.46	55.5	1.43
$1,4-R_2C_6H_4$[b]	85	5	55.5	1.46	55.8	1.35
$1,3,(4)-R_2(CH_3)C_6H_3$[b]	103–104 (16)	50	53.7	1.89	53.7	1.86
$1,3,(4),(5)-R_2(CH_3)_2C_6H_2$[b,c]	125–126 (15)	25	52.1	2.28	51.8	2.25
$1,3,(4),(6)-R_2(CH_3)_2C_6H_2$[b]	126–127 (16)	63	52.1	2.28	51.8	2.21
$1,4,(2),(5)-R_2(CH_3)_2C_6H_2$[b,c]	118–120	20	52.1	2.28	52.5	2.51
$4,4'-(RC_6H_4)_2$[c,d]	125.8–126.4	70	46.8	2.06	46.6	2.15
$4,4'-(RC_6H_4)_2CH_2$[c,d]	118–119 (2)	30	45.6	2.40	45.8	2.00

[a] Known; ref. 7. [b] Orientation confirmed by n.m.r. [c] Preferably prepared stepwise. [d] Orientation not proved experimentally; orientation of all other compounds proved by alkaline cleavage.

perature, the use of large quantities of catalyst did not have the desired effect, and at higher temperatures reaction occurred between the aluminum chloride and the bis alcohol forming high-melting solids of undetermined structure. The one-step procedure for preparing the bis compounds was successfully extended to other aromatic hydrocarbons, as noted in Table III. In some cases, however, best results were obtained by operating in two steps with intermediate isolation and purification of the mono compound.

The position of the entering 2-hydroxyhexafluoro-2-propyl groups with respect to the other ring substituents was established, except as indicated in Tables I and III, by alkaline cleavage to the corresponding carboxylic acid, and/or by examination of the proton n.m.r. values.

The infrared spectra of the 2-hydroxyhexafluoro-2-propyl compounds exhibited typical very sharp absorption at 2.65 to 2.75 μ for the unassociated hydroxyl group.[8] A broader band centering at about 3 μ indicated some degree of association in chloroform solution.

As indicated in Table IV, a proton n.m.r. structural study was made of ten of the compounds cited in Tables I and III. In all cases good agreement was found between the integrated values and the theoretical values for the number of protons corresponding to methyl, hydroxyl, and aryl types.

For xylenes substituted with either one or two 2-hydroxyhexafluoro-2-propyl groups, the methyl proton positions are between 2.22 and 2.24 for a methyl group nonadjacent to a fluorinated moiety. This value is similar to that for the methyl groups in the three xylene isomers. The compound, 1,3-bis(2-hydroxyhexafluoro-2-propyl)-4,5-dimethylbenzene, is exceptional, since the proton positions in the methyl group nonadjacent to the fluorinated group occur outside the given range at 2.38 p.p.m. In the xylene derivatives where a methyl group is *ortho* to a fluorinated moiety, the methyl proton positions are shifted downfield to between 2.4 and 2.6 p.p.m.

Hydroxyl proton peak positions were between 3.2 and 3.5 p.p.m. for all of the compounds studied, except 1,3-bis(2-hydroxyhexafluoro-2-propyl)-4-methylbenzene, which showed a split with peaks at 3.71 and 3.83 p.p.m.

Aromatic protons in the new compounds, adjacent to a methyl group or another proton, gave peak positions between 6.9 and 7.3 p.p.m. corresponding to approximately the normal position for the aromatic protons in the xylenes. A coupling constant of about 7 c.p.s. was obtained for two nonequivalent protons *ortho* to each other. This value is normal for two adjacent and nonequivalent aromatic protons.[9] Introduction of the 2-hydroxyhexafluoro-2-propyl group resulted in deshielding of the protons situated *ortho* to it, with resulting shifts to between 7.4 and 8.2 p.p.m.

The 2-hydroxyhexafluoro-2-propyl compounds have relatively strong acid character and are, therefore, soluble in aqueous sodium hydroxide. They can, in fact, be recovered unchanged even after refluxing several hours with 20% alcoholic sodium hydroxide. Under more drastic alkaline conditions, however, smooth haloform cleavage occurs to the corresponding carboxylic acid. This reaction, which proceeds in good yield and has proved useful for the identification of many of the compounds prepared in the present study, is the subject of a separate communication.[10] The hydroxyl group was exchanged for chlorine in 80% yield by refluxing with excess thionyl chloride and pyridine a technique used by Knunyants and co-workers[4] for

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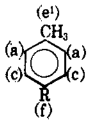
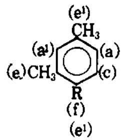
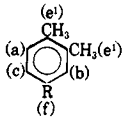
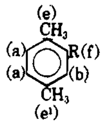
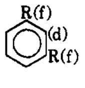
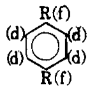
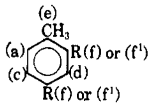
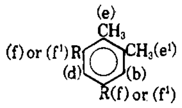
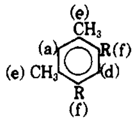
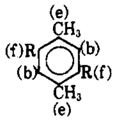
(8) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1959, p. 96.

(9) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, Inc., New York, N. Y., 1959.

(10) Perhalo Ketones. VIII. B. S. Farah, E. E. Gilbert, E. S. Jones, and J. A. Otto, *J. Org. Chem.*, **30**, 1006 (1965).

TABLE IV

N.M.R. DATA FOR AROMATIC HYDROCARBON DERIVATIVES OF HEXAFLUOROACETONE[a]

Compd.[b]	Proton chemical shifts in p.p.m.[c]								
	a	a^1	b	c	d	e	e^1	f	f^1
	7.24 7.11	..	..	7.77 7.63 7.52[d]	..	..	2.31	3.32	..
	7.05 6.94	7.05	..	7.53 7.41	..	2.43	2.22	3.40	..
	7.21 7.07	..	7.51	7.48 7.37	..	..	2.22	3.40	..
	7.08	..	7.51	..	..	2.52	2.24	3.39	..
	..[e]	..	..	..	8.22	..	..	3.50	..
	..	..	..	..	7.83[f]	..	..	3.70	..
	7.41 7.28	..	..	7.82 7.69	8.09	2.62	..	3.71	3.83
	..	..	7.48	..	7.83	2.55	2.38	3.55	3.47
	7.15	..	..	..	7.66	2.54	..	3.22	..
	..	..	7.42	..	..	2.60	..	3.25	..

[a] Tested as 20% by weight in carbon tetrachloride. [b] R denotes the 2-hydroxyhexafluoro-2-propyl moiety; (f) and (f^1) refer to the hydroxyl proton in this group. [c] Downfield from tetramethylsilane used as internal standard. [d] It is not clear whether this peak is due to an impurity or whether the pattern is not truly AB. [e] The three adjacent ring protons are indicated in the spectrum by a complex multiplet between 7.32 and 7.92 p.p.m. which is typical of an ABC pattern. [f] Deuteriochloroform was used as solvent.

analogous compounds. This replacement could not be effected by refluxing with phosphorus pentachloride in benzene. Acetylation of the fluoro alcohols occurred readily in refluxing acetic anhydride. These alcohols appear very stable thermally; 1-(2-hydroxyhexafluoro-2-propyl)naphthalene was recovered unchanged after refluxing at 300° for several hours.

Experimental

(2-Hydroxyhexafluoro-2-propyl)benzene.—Aluminum chloride (5 g.) was suspended in thiophene-free benzene (880 g., 11.3 moles) in a three-necked laboratory reaction flask equipped with stirrer, gas inlet tube, thermometer, reflux condenser cooled with Dry Ice–acetone, and external cooling bath. Hexafluoroacetone (b.p. −28°) was admitted with stirring and cooling at below 20° as fast as it was absorbed as indicated by reflux; 8 hr. was required for 1115 g. (6.72 moles) to react. The reaction mixture was water washed, dried, and distilled. The yield was 1541 g., 94% of theory.

Generally, similar conditions were used to prepare the other compounds in Tables I and II. In cases where a solid compound was used, 10 wt. of carbon disulfide was employed as solvent and the above procedure was followed. Reaction temperature did not appear critical in the area 10 to 40°, but in one case (4-chlorotoluene with *sym*-tetrafluorodichloroacetone) operation below 10° gave a long induction period followed by reaction of uncontrollable violence. Several attempts to employ nitrobenzene as solvent were unsuccessful, apparently because it undergoes complex formation with the catalyst.

1,3-Bis(2-hydroxyhexafluoro-2-propyl)benzene.—Benzene (78 g., 1 mole) and aluminum chloride (1 g.) were placed in a laboratory reaction flask equipped as described above, but also provided with a solid addition tube connected by wide flexible rubber tubing to a flask containing 20 g. of aluminum chloride. Hexafluoroacetone was admitted into the stirred reaction flask at such a rate that no refluxing was noted from the Dry Ice–acetone condenser. The temperature of the reaction mixture rose to about

50° and was maintained at 40 to 50° by the occasional addition of portions of catalyst through the solid addition tube whenever the temperature dropped to 40°. In several experiments, the total amount of aluminum chloride used varied from 6 to 20 g. A shorter reaction time is possible with comparatively larger amounts of catalyst, but a corresponding drop in yield was noted. Reaction times were 6 to 8 hr. for the absorption of 332 g. (2.0 moles) of hexafluoroacetone. The reaction mixture was decomposed promptly (to avoid decomposition) by dropwise addition of 500 ml. of cold water over 30 min. Chloroform (200 ml.) was added; the organic layer was separated, water-washed, dried, and distilled. The yield was 344 g., 84% of theory.

This general procedure was employed to prepare other compounds as noted in Table III. In several cases, as noted, it was found preferable to operate stepwise, with intermediate isolation of the pure mono derivative. Carbon disulfide was found a suitable solvent for preparing the bis derivatives, when using either one step or two.

Perhalo Ketones. VI. Aromatic Amino Derivatives of the Perhaloacetones

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Twenty-two new carbinols were prepared by condensing tetrafluorodichloro-, pentafluoromonochloro-, and hexafluoroacetones with various aromatic amines. Addition of *p*-toluenesulfonic acid catalyst reduces the reaction time and temperature and improves product yield with hexafluoroacetone, makes possible the isolation of definite products with the fluorochloroacetones, and induces reaction with amines of low basicity. N.m.r. structural studies were made on eight of the compounds.

Knunyants and co-workers have reported facile electrophilic attack of aniline and of its N-methyl derivatives[1,2] by anhydrous or hydrated hexafluoroacetone to form the corresponding bis(trifluoromethyl)-carbinols. The present study, part of a general pro-

$$C_6H_5NH_2 + (F_3C)_2CO \longrightarrow (F_3C)_2C(OH)C_6H_4NH_2$$

gram on reaction and derivatives of the perhaloacetones,[3] involves extension of this type of reaction to other aromatic amines and to other perhaloacetones. A method employed by Knunyants, involving direct treatment of the amine with anhydrous hexafluoroacetone at 170–200°, was found to proceed fairly satisfactorily with other aromatic amines to form the products listed in Table I.

When efforts to extend the reaction to tetrafluorodichloroacetone yielded only intractable tars, it was found that the use of a small quantity of *p*-toluenesulfonic acid as catalyst greatly facilitated reaction and made possible the isolation of the desired products (Table II), although in generally lower yields than noted with hexafluoroacetone. Lower yields have also been noted[3] in the aluminum chloride catalyzed condensation of aromatic hydrocarbons with the fluorochloroacetones as contrasted with hexafluoroacetone. Both of these effects are explainable by lowered electrophilic character and consequent reduced reactivity of the carbonyl carbon as fluorine is replaced by chlorine, and

TABLE I

AROMATIC AMINO DERIVATIVES OF HEXAFLUOROACETONE

Amine used	Yield, %[a]	M.p., °C.[b]	Isomer[c]	% C Calcd.	% C Found	% H Calcd.	% H Found	% N Calcd.	% N Found
Aniline	60	151.5–152.5[d]	*p*[e,f]	41.7	41.2	2.7	2.5	...	...
2-Toluidine	47	136–137	*p*[e,f]	44.0	44.0	3.3	3.3	5.1	5.0
3-Toluidine	54	104–106	*o*[e–g]	44.0	43.8	3.3	3.1	5.1	5.4
4-Toluidine	55	109–110	*o*[e]	44.0	43.3	3.3	3.1	5.1	5.1
2,4-Dimethylaniline	45	113–114	*o*[f]	46.0	45.9	3.9	3.3	4.9	5.0
2,5-Dimethylaniline	61	162.5–163.5	*p*[f]	46.0	45.7	3.9	3.3	4.9	4.7
2,6-Dimethylaniline	66	174–175	*p*[e,f]	46.0	46.1	3.9	3.8	4.9	5.2
N-Methylaniline	55	89–90[h]	*p*[f]	44.0	43.8	3.3	2.9	5.1	5.1
N,N-Dimethylaniline[i]	58	79–80[j]	*p*	46.0	46.0	3.9	3.3	4.9	5.1
2-Methoxyaniline	29	129–130	*p*[e,f]	41.5	41.7	3.1	3.3	4.8	4.8
2-Chloroaniline[k]	30	122–123	*p*[l]	36.8	37.2	2.1	2.4	4.8	4.6
3-Chloroaniline[k,m]	27	84–86	*p*[l]	34.9	35.5	2.0	2.4	4.5	4.4
2-Hydroxyaniline	19	170–171	*p*[e]	39.3	38.9	2.6	2.7	5.1	4.9
2-Aminobiphenyl[k]	57	143–144	*p*[l]	53.7	54.2	3.3	3.7	4.2	4.4
4-Aminobiphenyl[k]	31	165–166	*o*[l]	53.7	53.7	3.3	2.5	4.2	4.1
1-Naphthylamine	60	164.5–165.5	*o*[e]	50.5	50.2	2.9	2.5	4.5	4.5
Acetanilide[i]	31	156–158	*p*[n]	43.9	43.8	3.0	3.6	4.7	5.0

[a] Of once-recrystallized product, based on either reagent. [b] Uncorrected. [c] Indicates position of the 2-hydroxyperhalo-2-propyl moiety with respect to the amino group. [d] Ref. 2 gives 151–152°. [e] Proved by hydrolysis to the carboxylic acid. [f] As indicated by n.m.r. [g] 1-(2-Hydroxyhexafluoro-2-propyl)-2-amino-4-methylbenzene. [h] Ref. 1a gives 87–89°. [i] $AlCl_3$ used as catalyst. [j] Ref. 1a gives 75–176°. [k] *p*-Toluenesulfonic acid catalyst added; otherwise no catalyst was used. [l] Orientation not proven. [m] Pentafluorochloroacetone used. [n] Proved by hydrolysis to 1-(2-hydroxyhexafluoro-2-propyl)-4-aminobenzene.

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