

of the solid products were isolated from the reaction mixtures and identified by mixture melting points. All melting points are corrected.

Pentafluoriodobenzene and Nickel Carbonyl in THF.—Pentafluoriodobenzene (29 g, 0.1 mole) was refluxed with nickel carbonyl (17 g, 0.1 mole) in 50 ml of THF until the boiling point of the mixture had reached 67°. The dark solution was diluted with water (200 ml) and hydrochloric acid (10 ml), extracted with benzene, and dried (Na_2SO_4); the benzene was distilled on a steam bath. The remaining oil was distilled *in vacuo* using a short column giving pentafluoriodobenzene (17.2 g, 59%). Repeated recrystallization of the residue from heptane gave II (2.5 g, 37%), mp 69°–70°. Evaporation of the mother liquor gave an oily residue; its infrared spectrum showed a band in the 1700- cm^{-1} region ($\text{C}_6\text{F}_5\text{-C=O}$).

Pentafluoriodobenzene and Nickel Carbonyl in DMF.—Pentafluoriodobenzene (55 g, 0.189 mole) and nickel carbonyl (32 g, 0.187 mole) in DMF (30 ml) were gently refluxed on a steam bath. After refluxing for 6 hr, the cooled mixture was diluted with water (150 ml), the organic layer separated, and the aqueous layer was extracted several times with benzene. The combined organic layers were washed with water and dried (Na_2SO_4); the benzene was distilled on a steam bath. Distillation of the remaining oil using a short column *in vacuo* gave pentafluoriodobenzene (20 g, 36%). The residue was recrystallized from ethanol giving II (6.36 g), mp 69.5–70°. After evaporation of the ethanol, the remaining residue was twice recrystallized from heptane giving III (4.3 g). Additional II (1.64 g) and III (1.37 g) were isolated from the mother liquor by chromatography on alumina. The over-all yields based on consumed pentafluoriodobenzene were 8.0 g of II (40%) and 5.67 g of III (26.3%).

Pentafluoriodobenzene and Nickel Carbonyl in Toluene.*—Pentafluoriodobenzene (12 g, 0.041 mole), nickel carbonyl (7.26 g, 0.0425 mole), and toluene (100 ml) were refluxed for 5 hr on a steam bath. Dilute hydrochloric acid (50 ml, 5%) was added to the cooled mixture, the organic phase separated, the aqueous layer was extracted with toluene (10 ml), and the extract was combined with the organic phase and dried (CaCl_2). Gas chromatography showed these yields (compound, g, %): I, 0.602, 23.2; II, 0.91, 35.2; III, 0.57, 20.4 (unreacted pentafluoriodobenzene 7.45 g, 62.1%). Another run under similar conditions, but which was heated more slowly, gave the following total yields (compound, g, %): I, 0.55, 19.6; II, 0.74, 26.6; III, 0.53, 17.6 (unreacted pentafluoriodobenzene, 7.1 g, 59.2%).

Pentafluoriodobenzene with Excess Nickel Carbonyl.*—Pentafluoriodobenzene (12 g, 0.041 mole) and nickel carbonyl (39.6 g, 0.232 mole) were refluxed for 3 hr. After removal of most of the excess nickel carbonyl by distillation, the mixture was treated with hydrochloric acid (20 ml, 5%), and the organic layer was separated and dried. Gas chromatography showed the following yields (compound, g, %): II, 0.724, 31.6; III, 0.844, 34.0 (unreacted pentafluoriodobenzene, 7.97 g, 66.4%).

Pentafluoriodobenzene and Toluene.*—Pentafluoriodobenzene (12 g, 0.041 mole) and toluene (100 ml) were refluxed and worked up as described above. No I or II could be detected by gas chromatography. Pentafluoriodobenzene (10.7 g, 89.2%) was recovered by fractional distillation.

Pentafluorobromobenzene and Nickel Carbonyl in DMF.—Pentafluorobromobenzene (51.6 g, 0.209 mole) and nickel carbonyl (36.75 g, 0.215 mole) in DMF (50 ml) were treated as described above for pentafluoriodobenzene. From the reaction mixture were isolated unreacted pentafluorobromobenzene (38.2 g, 74%), II (1.13 g, 12.5%), and III (2.86 g, 29.1%).

Pentafluorobromobenzene with Excess Nickel Carbonyl.*—Pentafluorobromobenzene (10.08 g, 0.041 mole) and nickel carbonyl (39.6 g, 0.23 mole) were treated as described above for pentafluoriodobenzene. The investigation of the residue by gas chromatography showed the presence of unreacted pentafluorobromobenzene (88%), II (<5%), and III (<5%). The exact yields of the latter two products were not determined.

Hexafluorobenzene and Nickel Carbonyl in DMF.—Hexafluorobenzene (42.32 g, 0.228 mole) and nickel carbonyl (39.21 g, 0.229 mole) in DMF (20 ml) were treated as described above. Only hexafluorobenzene (39 g, 92%) and some pyrophoric nickel were isolated from the reaction mixture.

Registry No.—Pentafluoriodobenzene, 827-15-6; pentafluorobromobenzene, 344-04-7; hexafluorobenzene, 392-56-3; II, 434-90-2.

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Highly Acidic Perhalogenated Alcohols. A New Synthesis of Perfluoro-*t*-butyl Alcohol

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Perfluoro-*t*-butyl alcohol (I) has been the subject of controversy with regard to its method of preparation and its acidity. It has been claimed^{2a} that hexafluoroacetone reacts with trifluoromethylmagnesium iodide to give I, $\text{p}K_a = 9.52$.^{2b} This method has never been confirmed.

Recently, Knunyants³ synthesized I by an arduous route, involving oxidation of $(\text{CF}_3)_3\text{CNO}$ to $(\text{CF}_3)_3\text{CONO}$ and hydrolysis of the nitrite, and reported the much more acidic $\text{p}K_a = 5.4$.

We now report a more direct method for the preparation of I and related perhalogenated tertiary alcohols and confirm the $\text{p}K_a$ value of Knunyants. The reactions are outlined as shown in Scheme I.

Trichloromethylithium⁴ reacts with hexafluoroacetone at -100° to yield, after acidification, complex II. Trichloromethyl bistrifluoromethylcarbinol (III) is isolated in 50% yield by distillation from concentrated sulfuric acid.

Compound III reacts with an excess of antimony pentafluoride in a steel bomb heated at 80° for 16 hr. After work-up of the reaction mixture, a 60% yield of perfluoro-*t*-butyl alcohol (I) is obtained. When III is treated with SbF_3 and SbCl_5 , a 45% yield of alcohol IV is obtained (Scheme I).

The $\text{p}K_a$ values of I, III, and IV, determined by potentiometric titration (Table I), reveal the powerful polar effect of three perhalomethyl groups in enhancing the acidity. Our results confirm those of Knunyants and clearly indicate that Haszeldine did not prepare compound I, and that the frequently quoted^{5,6} $\text{p}K_a$ value is erroneous.

Further evidence of the high acidity of these alcohols is found by comparing infrared stretching frequencies of unbonded OH in CCl_4 with the bonded frequencies in tetrahydrofuran. The larger the difference ($\Delta\lambda$), the stronger is the hydrogen bond to THF. An excellent linear relationship exists between the acidities of these and similar alcohols and the strengths of the hydrogen bonds (Table I). The alcohols react slug-

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(2) (a) R. N. Haszeldine, 122nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1952, Abstracts, p 13K, and in oral presentation. This author has not published a $\text{p}K_a$ value for I. (b) A. M. Lovelace, D. A. Rausch, and W. Postelnek, "Aliphatic Fluorine Compounds," Reinhold Publishing Corp., New York, N. Y., 1958, p 138.

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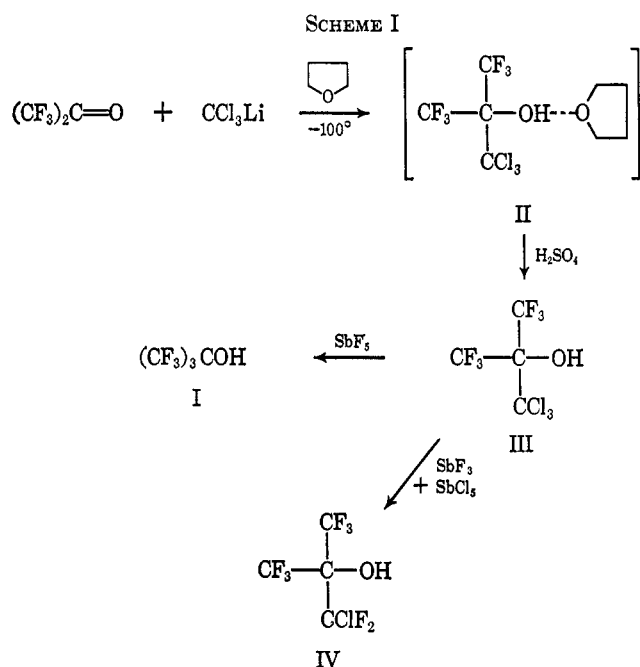


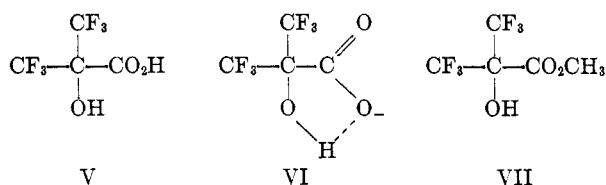
TABLE I
ACIDITIES OF HALOGENATED ALCOHOLS AND CARBONYL
FREQUENCIES OF THEIR ACETATE ESTERS

Alcohol (ROH)	pK_a (25°)	$\Delta\lambda_{\text{OH}}$, μ	$\nu_{\text{C}=\text{O}}^a$ (cm^{-1}) of ($\text{CH}_3\text{CO}_2\text{R}$)
$\text{CF}_3\text{CH}_2\text{OH}$	12.4	0.22	1768
$(\text{CF}_3)_2\text{C}(\text{CH}_3)\text{OH}$	9.6	0.32	1780
$(\text{CF}_3)_2\text{CHOH}$	9.3	0.35 ^b	1792
$(\text{CF}_3)_2\text{C}(\text{CClF}_2)\text{OH}$	5.3	0.49	
$(\text{CF}_3)_3\text{COH}$	5.2	0.50	1820
$(\text{CF}_3)_2\text{C}(\text{CCl}_3)\text{OH}$	5.1	0.51	1817

^a CCl_4 solution. ^b Reference 5.

gishly with excess acetyl chloride in the presence of aluminum chloride to give, after extraction with ether, azeotropic mixtures of alcohol-ether complex and acetate ester, which are difficult to separate. The carbonyl frequencies of these impure esters are found at the highest frequencies ever recorded for compounds of this type, *viz.* 1820 cm^{-1} . A detailed discussion of this effect will be presented in a forthcoming paper.

We also prepared hydroxy acid V⁷ by sulfuric acid hydrolysis of the potassium salt of the cyanohydrin of hexafluoroacetone. The pK_a of V is 2.1, but the OH



group fails to exhibit acidic properties. We ascribe this behavior to intramolecular hydrogen bonding (VI), which enhances the acidity of the carboxyl group while suppressing that of the OH group. In the methyl ester (VII), such bonding is precluded and the high acidity ($pK_a = 7.7$) of the OH group becomes apparent. Middleton and Lindsey⁵ explained the acidity ($pK_a = 5.95$) of perfluoropinacol on similar grounds. While hydrogen bonding doubtless makes some con-

tribution, its importance in this case was grossly exaggerated, since the erroneous value for I was used as reference.

Experimental Section

Preparation of Trichloromethylbistrifluoromethylcarbinol (III).—To a dry, 500-ml, three-necked flask fitted with a stirrer, Dry Ice condenser, and dropping funnel was added 300 ml of anhydrous tetrahydrofuran and 33.0 g (214 mmoles) of carbon tetrachloride under an atmosphere of dry nitrogen. The mixture was then cooled to -110° in an ether-liquid nitrogen bath. At this time, 133 ml (215 mmoles) of *n*-butyllithium in hexane was added dropwise to the stirred solution during a period of 90 min. After an additional 0.5 hr, 35.5 g (214 mmoles) or hexafluoroacetone was slowly bubbled into the reaction mixture. At the end of 1 hr after the addition of hexafluoroacetone was complete, the reaction mixture was allowed to warm slowly to room temperature. Stirring was discontinued and the solvent was stripped off (rotary evaporator). After acidification with 10% hydrochloric acid, the residue was extracted with ether. The ether layer was dried over sodium sulfate and distilled to give a mixture of the 1:1 complex of tetrahydrofuran and alcohol (II) and the free alcohol (III).

The tetrahydrofuran was removed by distilling the complex from concentrated sulfuric acid. The distillate was redistilled to give 30 g (50% yield) of pure trichloromethylbistrifluoromethylcarbinol (III) as a colorless, volatile liquid, bp 136–137°. The OH absorption was found at τ 6.04 (neat) in the nmr and at 3570 cm^{-1} (CCl_4) in the infrared.

Anal. Calcd for $\text{C}_4\text{HCl}_3\text{F}_6\text{O}$: Cl, 37.27; mol wt, 285.4. Found: Cl, 36.80; mol wt, 285 (neut equiv).

Preparation of Perfluoro-*t*-butyl Alcohol (I).—A mixture of 10.0 g of III and 39.0 g (5 molar excess) of antimony pentafluoride was heated in a steel bomb at 65–80° with shaking for 16 hr. After cooling the bomb, the excess SbF_5 was decomposed by spraying 15 ml of ice-cold water into the contents of the bomb. The mixture was then washed with ice-cold 10% hydrochloric acid and extracted with ether, and the ether layer was washed with hydrochloric acid. The ether layer was dried over sodium sulfate and distilled to give the 1:1 ethyl ether-alcohol complex, boiling range 65–85°. Pure perfluoro-*t*-butyl alcohol (I, 5.0 g, 60% yield, bp 44–45°) was obtained by distilling the complex from concentrated sulfuric acid. The OH absorption was found at τ 6.34 (neat) in the nmr and at 3610 cm^{-1} (CCl_4) in the infrared.

Anal. Calcd for $\text{C}_4\text{HF}_9\text{O}$: C, 20.35; H, 0.43; F, 72.44. Found: C, 20.30; H, 0.45; F, 71.82.

Preparation of Difluorochloromethylbistrifluoromethylcarbinol (IV).—A mixture of 10.0 g of III, 30.0 g (3 molar excess) of antimony trifluoride, and 15 ml of antimony pentachloride was heated in a steel bomb at 150° with shaking for 12 hr. After cooling the bomb, the mixture was washed with ice-cold 10% hydrochloric acid and extracted with ether, and the ether layer was washed with hydrochloric acid. The ether layer was dried over sodium sulfate and distilled to give the 1:1 ethyl ether-alcohol complex, boiling range 75–95°. Distillation of the complex from concentrated sulfuric acid gave 4.0 g (45% yield) of difluorochloromethylbistrifluoromethylcarbinol (IV), bp 73–75°. The OH absorption was found at τ 6.28 (neat) in the nmr and at 3610 cm^{-1} (CCl_4) in the infrared.

Anal. Calcd for $\text{C}_4\text{HClF}_3\text{O}$: Cl, 14.04. Found: Cl, 13.80.

Preparation of Bistrifluoromethylglycolic Acid (V).—To a dry, 500-ml, three-necked flask equipped with a Dry Ice condenser, dropping funnel, and stirrer was added 190 ml of anhydrous ethyl ether, 10 ml of anhydrous tetrahydrofuran, and 9.0 g (138.4 mmoles) of potassium cyanide under an atmosphere of dry nitrogen. After the mixture was cooled to -25° , 23 g of hexafluoroacetone (138.4 mmoles) was slowly bubbled into the suspension. The mixture was then slowly warmed to room temperature and allowed to react for 1 additional hr. The crude potassium salt of the cyanohydrin of hexafluoroacetone (30 g, 95%) was isolated after evaporation of the solvent and was used without further purification.

The potassium salt of the cyanohydrin of hexafluoroacetone (30 g) was added slowly to a 250-ml, round-bottom flask containing 150 ml of concentrated sulfuric acid and the mixture was heated under reflux at 160–180° for 24 hr. Pure, hygroscopic bistrifluoromethylglycolic acid (V, 13 g, 60% yield, bp 153–156°, mp 82–85°) was obtained by distillation from the reaction

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