A similar experiment using aluminum chloride (B) after 21 hr of refluxing gave II (17.0 g, 33%, based upon chloroform).

B. With Cupric Chloride.—A mixture as described above, using aluminum chloride (F), was refluxed together with anhydrous cupric chloride (1.3 g, 0.01 mole) for 1.5 hr. Work-up of the dark red mixture gave II (30.7 g, 59%, based upon chloroform).

C. With Copper Powder.—A mixture as described under B, but with copper powder (1 g) substituted for cupric chloride, was refluxed for 1.5 hr. Work-up of the violet-red mixture gave II (30.2 g, 58%, based upon chloroform).

Pentafluorophenylphenylmethane (IV).—To a stirred mixture of benzene (15.6 g, 0.2 mole) and aluminum chloride (F) (2.67 g, 0.02 mole) was added dropwise 2,3,4,5,6-pentafluorobenzyl chloride (2.17 g, 0.01 mole)[16] at room temperature. The mixture immediately became warm and evolved hydrogen chloride. After refluxing for 2.5 hr the reddish brown mixture was worked up as described giving IV (1.65 g, 64%, based upon pentafluorobenzyl chloride), mp 56–57° (ethanol); ν_{max} (CCl_4) 3101 sh, 3085, 3062, 3028, 2939, 2873, 2853, 2633, 2472, 2412, 2068, 1956, 1941, 1873, 1797, 1721, 1651, 1601, 1514, 1500, 1452, 1420, 1372, 1302, 1291, 1181, 1121, 1079, 1030, 995, 961, 916, 899, 724, 697, 661, 608 cm^{-1}; λ_{max}^{I} 217 sh mμ (ε 10,332), 252 (1053), 258 (789), 263 sh (656), 268 sh (413), 306 (102). The proton nmr spectrum consisted of a triplet centered at τ 5.83 (aliphatic). The F^{19} nmr spectrum in acetone consisted of multiplets centered at 1199 (*ortho*), 370 (*para*, triplet), 82 (*meta*) cps, downfield from hexafluorobenzene singlet. *Anal.* Calcd for $C_{13}H_7F_5$: C, 60.47; H, 2.73; F, 36.79. Found: C, 60.47; H, 2.61; F, 36.94.

Registry No.—Pentafluorobenzene, 363-72-4; III, 771-56-2; I, 5736-46-9; II, 4780-60-3; IV, 7484-19-7.

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Notes

Nickel Carbonyl Reaction with Pentafluorohalobenzenes[1,2]

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It is well established that certain metal carbonyls react with aliphatic halides causing polymerization of olefinic compounds *via* a radical mechanism.[3] Little is known about the reaction of metal carbonyls with aromatic halides. Bauld[4] recently reported that nickel carbonyl with iodobenzene in aprotic solvents (THF is preferred) gave benzil in good yield.

This Note reports our effort to use the reaction of nickel carbonyl with pentafluoroiodobenzene as a synthetic route for the formation of decafluorobenzil.

Refluxing pentafluoroiodobenzene with nickel carbonyl in various solvents failed to produce decafluorobenzil. In an experiment with THF as the solvent, an oily residue was isolated; its infrared spectrum exhibited an intense absorption band in the 1710–1700-cm^{-1} region characteristic of the pentafluorobenzoyl group. When the experiments were carried out in dimethylformamide (DMF), toluene, and excess nickel carbonyl as solvents, decafluorobiphenyl, decafluorobenzophenone, and pentafluorobenzene were isolated as the only reaction products. The experimental results are summarized in Table I.

The mechanism proposed by Bauld[4] for the reaction of iodobenzene with nickel carbonyl[5] evidently cannot explain our results with pentafluoroiodobenzene.

In our study with pentafluoroiodobenzene, a radical mechanism involving pentafluorophenyl radicals must be predominant. The evidence which leads to this conclusion is as follows.

(1) From all reactions which were run in the presence of nickel carbonyl, both decafluorobiphenyl and decafluorobenzophenone were isolated. This result does not exclude an Ullmann-type reaction between metallic nickel (from decomposed nickel carbonyl) and pentafluoroiodobenzene, but an Ullmann reaction would only explain the formation of decafluorobiphenyl, not that of decafluorobenzophenone and pentafluorobenzene.

(2) The ratio decafluorobiphenyl to decafluorobenzophenone is about equal in the nonpolar solvent toluene and the polar solvent DMF. If a mixed ionic–radical mechanism were involved, the ratio of the products formed in the polar solvent should be distinctly different in favor of the decafluorobenzophenone, which is not the case. Only in nickel carbonyl as solvent, the decafluorobiphenyl/decafluorobenzophenone ratio is shifted in favor of the latter. A reasonable explanation is that the initially formed pentafluorophenyl radicals are surrounded by a large excess of nickel carbonyl molecules and therefore have a higher chance of carbonylation.

The generation of pentafluorophenyl radicals during the reaction is indicated by the formation of pentafluorobenzene (abstraction of hydrogen from the solvent by pentafluorophenyl radicals), decafluorobiphenyl

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[1] This work was supported by the Foundational Research Program of the Naval Ordnance Systems Command.

[2] Presented in part at the 3rd International Fluorine Chemistry Symposium, Munich, Germany, Sept 1965.

[3] H. Kröper and H. M. Weitz, German Patent 1,051,003 (1959); *Chem. Abstr.*, **55**, P2181 (1961); C. H. Bamford, R. Denyer, and G. C. Eastmond, *Trans. Faraday Soc.*, **61**, 1499 (1965), and references cited therein.

[4] N. L. Bauld, *Tetrahedron Letters*, 1841 (1963).

[5] Bauld[4] explained the formation of benzil by intermediate formation of a complex C_6H_5–Ni(I)$(CO)_n$ followed by a subsequent bimolecular step. The presence of free aryl and aroyl radicals was excluded in his mechanistic considerations because the yields of aril were not substantially diminished when the reactions were run in the presence of large excesses of cyclohexene and benzaldehyde, two radical scavengers.

TABLE I[a]

RESULTS FROM THE REACTION OF PENTAFLUOROHALOBENZENE WITH NICKEL CARBONYL

C_6F_5X, X =	C_6F_5X–$Ni(CO)_4$	Solvent	C_6F_5X recovd, %	C_6F_5H, %	C_6F_5–C_6F_5, %	$C_6F_5COC_6F_5$, %	$\frac{C_6F_5-C_6F_5}{C_6F_5COC_6F_5}$
I	1:1	DMF	36	*f*	40	26.3	1.52
I[b,c,d]	1:1.04	$C_6H_5CH_3$	62.1	23.2	35.2	20.4	1.73
I[b,d,e]	1:1.04	$C_6H_5CH_3$	59.2	19.6	26.6	17.6	1.51
I[b,d]	1:5.64	$Ni(CO)_4$	66.4		31.6	34.0	0.93
Br	1:1	DMF	74	*f*	12.5	29.1	0.43
Br[b,d]	1:5.64	$Ni(CO)_4$	88		<5	<5	
F	1:1	DMF	92		0	0	
I[b]	No $Ni(CO)_4$	$C_6H_5CH_3$	89.2	0	0		

[a] The yields of C_6F_5H, $C_6F_5C_6F_5$, and $C_6F_5COC_6F_5$ are based on consumed C_6F_5X. [b] The experiments were carried out under nitrogen. [c] The mixture was quickly heated to reflux temperature. [d] The yields were determined by gas chromatography. [e] The mixture was slowly heated to reflux temperature. [f] Not determined.

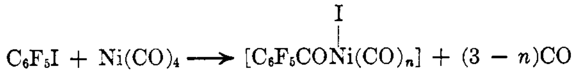
(combination of two pentafluorophenyl radicals), and by the independence of the ratio of decafluorobiphenyl/decafluorobenzophenone to the reaction solvent. The radicals could be produced either directly by the reaction of pentafluoroiodobenzene with nickel carbonyl (*via* the complex $[C_6F_5\text{–}Ni(I)(CO)_n]$), or appear as a decomposition product of initially formed pentafluorobenzoyl radicals. The formation of decafluorobenzophenone is then explained either by an attack of the pentafluorophenyl radicals on dissolved carbon monoxide or on nickel carbonyl itself, forming pentafluorobenzoyl radicals which would react with pentafluorophenyl radicals (eq 1), or by the reaction of primarily formed pentafluorobenzoyl radicals with pentafluorophenyl radicals which in turn are derived from the decomposition of pentafluorobenzoyl radicals (eq 2).

$$C_6F_5\cdot \xrightarrow{\text{CO or } Ni(CO)_4} C_6F_5CO\cdot \xrightarrow{C_6F_5\cdot} C_6F_5COC_6F_5 \quad (1)$$

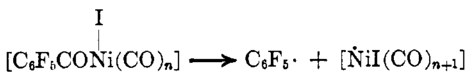
$$C_6F_5CO\cdot \xrightarrow[-CO]{} C_6F_5\cdot \xrightarrow{C_6F_5CO\cdot} C_6F_5COC_6F_5 \quad (2)$$

The absence of decafluorobenzil among the reaction products indicates that the reactive pentafluorobenzoyl radicals which are present in low concentration are consumed in other reactions before they have an opportunity to dimerize.

As a consequence of the experimental results, the reaction mechanisms shown in eq a–f seems to be most probable.



$$C_6F_5I + Ni(CO)_4 \longrightarrow [C_6F_5CO\overset{I}{\overset{|}{N}}i(CO)_n] + (3 - n)CO \quad (a)$$

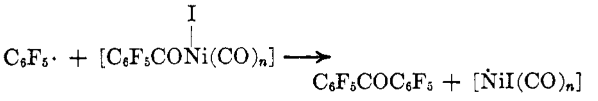


$$[C_6F_5CO\overset{I}{\overset{|}{N}}i(CO)_n] \longrightarrow C_6F_5\cdot + [\dot{N}iI(CO)_{n+1}] \quad (b)$$

$$C_6F_5\cdot + RH \longrightarrow C_6F_5H + R\cdot \quad (c)$$

$$2C_6F_5\cdot \longrightarrow C_6F_5\text{–}C_6F_5 \quad (d)$$

$$C_6F_5\cdot + [CO] \rightleftarrows C_6F_5\text{–}CO\cdot \quad (e1)$$



$$C_6F_5\cdot + [C_6F_5CO\overset{I}{\overset{|}{N}}i(CO)_n] \longrightarrow C_6F_5COC_6F_5 + [\dot{N}iI(CO)_n] \quad (e2)$$

$$C_6F_5CO\cdot + C_6F_5\cdot \longrightarrow C_6F_5COC_6F_5 \quad (f)$$

The generation of pentafluorophenyl radicals by a radical decomposition of pentafluoroiodobenzene by heat or light (as it is known for iodobenzene[6]) could be ruled out, because refluxing pentafluoroiodobenzene with toluene for several hours produced neither pentafluorobenzene nor decafluorobiphenyl.

Pentafluorobromobenzene, as expected, is less reactive toward nickel carbonyl than pentafluoroiodobenzene. With DMF as solvent, 74% of the pentafluorobromobenzene was recovered, the reaction products being decafluorobiphenyl and decafluorobenzophenone in a ratio of 1:2.3, while with excess nickel carbonyl as solvent a combined yield of less than 10% of decafluorobiphenyl and decafluorobenzophenone was obtained.

Again, the formation of perfluorobiphenyl in the reaction with pentafluorobromobenzene indicates a radical mechanism. This demonstrates the difference between the phenyl and the pentafluorophenyl group, as Bauld[4] found that bromobenzene did not react at all with nickel carbonyl in various solvents at temperatures ranging up to 140°.

Hexafluorobenzene did not react at all with nickel carbonyl in DMF; 92% hexafluorobenzene could be recovered unchanged.

Thus, although the preparation of decafluorobenzil failed, decafluorobenzophenone could be prepared by this method in reasonable yields. It has formerly been prepared by oxidation of bis(pentafluorophenyl)carbinol[7] or bis(pentafluorophenyl)methane,[8] by the reaction of pentafluorophenylmagnesium chloride with methyl chloroformate,[9] or by thermal decomposition of silicon tetrakis(pentafluorobenzoate),[10] but these methods give either low yields, or the starting materials are not easily obtained.

Experimental Section

All reactions marked with an asterisk were carried out under nitrogen. Nickel carbonyl and toluene were distilled under N_2 before use. The yields of pentafluorobenzene (I), decafluorobiphenyl (II), and decafluorobenzophenone (III) were based on consumed pentafluoroiodobenzene and -bromobenzene, respectively.

A 1-m silicon grease column in a Perkin-Elmer Model 154 vapor fractometer at 100° was used in the determination of pentafluorobenzene, pentafluorobromobenzene, and pentafluoroiodobenzene; the same column was used at 125° in the determination of decafluorobiphenyl and decafluorobenzophenone. The quantitative results were established by comparison with known mixtures of about similar composition. In all cases, samples

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[6] I. P. Gragerov and M. Ya. Turkina, *Dokl. Akad. Nauk SSSR*, **140**, 1317 (1961); *cf. Chem. Abstr.*, **56**, 9608*g* (1962); W. Wolf and N. Kharasch, *J. Org. Chem.*, **30**, 2493 (1965).

[7] A. K. Barbour, *et al.*, *J. Chem. Soc.*, 808 (1961); J. C. Tatlow, British Patent 923,115 (1963); *Chem. Abstr.*, **59**, 9902 (1963).

[8] W. F. Beckert and J. U. Lowe, Jr., unpublished results.

[9] N. N. Vorozhtsov, *et al.*, *Dokl. Akad. Nauk SSSR*, **159**, 125 (1964).

[10] P. Sartori and M. Weidenbruch, *Angew. Chem.*, **77**, 1077 (1965).

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

Pentafluoroiodobenzene and Nickel Carbonyl in THF.—Pentafluoroiodobenzene (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 pentafluoroiodobenzene (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 (C_6F_5–C=O).

Pentafluoroiodobenzene and Nickel Carbonyl in DMF.—Pentafluoroiodobenzene (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 pentafluoroiodobenzene (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 pentafluoroiodobenzene were 8.0 g of II (40%) and 5.67 g of III (26.3%).

Pentafluoroiodobenzene and Nickel Carbonyl in Toluene.*—Pentafluoroiodobenzene (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 pentafluoroiodobenzene 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 pentafluoroiodobenzene, 7.1 g, 59.2%).

Pentafluoroiodobenzene with Excess Nickel Carbonyl.*—Pentafluoroiodobenzene (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 pentafluoroiodobenzene, 7.97 g, 66.4%.)

Pentafluoroiodobenzene and Toluene.*—Pentafluoroiodobenzene (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. Pentafluoroiodobenzene (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 pentafluoroiodobenzene. 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 pentafluoroiodobenzene. 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.—Pentafluoroiodobenzene, 827-15-6; pentafluorobromobenzene, 344-04-7; hexafluorobenzene, 392-56-3; II, 434-90-2.

Acknowledgment.—We acknowledge the helpful discussions of Dr. W. E. McQuistion and Dr. M. Cziesla.

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, $pK_a = 9.52$.[2b] This method has never been confirmed.

Recently, Knunyants[3] synthesized I by an arduous route, involving oxidation of $(CF_3)_3CNO$ to $(CF_3)_3CONO$ and hydrolysis of the nitrite, and reported the much more acidic $pK_a = 5.4$.

We now report a more direct method for the preparation of I and related perhalogenated tertiary alcohols and confirm the pK_a value of Knunyants. The reactions are outlined as shown in Scheme I.

Trichloromethyllithium[4] 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 pK_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] pK_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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[1] National Aeronautics and Space Administration Fellow, Illinois Institute of Technology, 1964–1966.

[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 pK_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.

[3] I. L. Knunyants and B. L. Dyatkin, *Izv. Akad. Nauk USSR, Chem. Ser.*, 923 (1964).

[4] D. F. Hoeg, D. I. Lusk, and A. L. Crumbliss, *J. Am. Chem. Soc.*, **87**, 4147 (1965).

[5] W. J. Middleton and R. V. Lindsey, Jr., *ibid.*, **86**, 4948 (1964).

[6] D. P. Graham and V. Weinmayr, *J. Org. Chem.*, **31**, 957 (1966).