Anal. Calcd for $C_7H_{12}O_2$: C, 65.63; H, 9.38. Found: C, 65.63; H, 9.50.

Octanolid (8-hydroxyoctanoic acid lactone) has bp 76–76.5° (13.5 mm) (lit.[2] bp 72–73° (10.5 mm)), $n^{26}{}_D$ 1.4580, $n^{22}{}_D$ 1.4595.

Anal. Calcd for $C_8H_{14}O_2$: C, 67.61; H, 9.86. Found: C, 67.39; H, 9.95.

Nonanolid (9-hydroxynonanoic acid lactone) has bp 92° (12 mm) (lit.[2] bp 86–87° (10.5 mm)), $n^{26}{}_D$ 1.4652, $n^{24}{}_D$ 1.4660, $n^{21}{}_D$ 1.4673.

Anal. Calcd for $C_9H_{16}O_2$: C, 69.23; H, 10.26. Found: C, 69.12; H, 10.38.

Dodecanolid (12-hydroxydodecanoic acid lactone) has bp 119–120° (5 mm) (lit.[2] bp 130° (10.5 mm)), $n^{23}{}_D$ 1.4698, $n^{20}{}_D$ 1.4709.

Anal. Calcd for $C_{12}H_{22}O_2$: C, 72.73; H, 11.11. Found: C, 72.35; H, 11.19.

Hexamethylene adipate was prepared after the general procedure of Spanagel and Carothers.[18] Chromatographing the product twice on Florosil gave mp 68–70° (lit.[18] mp 70°).

Anal. Calcd for $C_{12}H_{20}O_4$: C, 63.14; H, 8.83. Found: C, 62.95; H, 8.71.

Hexamethylene azelate was prepared in similar fashion,[18] mp (after chromatography on Florosil) 54–56° (lit.[18] mp 59°).

Anal. Calcd for $C_{15}H_{26}O_4$: C, 66.64; H, 9.69. Found: C, 66.75; H, 9.85.

Spectroscopic Measurement.—All spectra were measured with a Cary recording spectrophotometer, Model 14, using matched 0.1-cm quartz cells. The details of the technique have been described previously.[5] The precision of measurement was at least ±5 A, and usually ±3 A, except where otherwise noted. Molar absorptivities were reproducible to at least ±5%. The oscillator strengths (*f*) of a few of the $n \rightarrow \pi^*$ transitions in isooctane were determined by a method described before.[19] The values follow: heptanolid, $f = 0.0019$; nonanolid, $f = 0.0019$; dodecanolid, $f = 0.0018$. These are very similar to the value previously found for *n*-butyl acetate in methanol (0.0017).[5] The values of *f* determined by this technique are probably in error by no more than 5% due to overlap of the weak band by the nearby allowed transition. Only a single smooth maximum in the $n \rightarrow \pi^*$ region was observed in each case.

---

[18] E. W. Spanagel and W. H. Carothers, *ibid.*, **57**, 939 (1935).

[19] Reference 5, footnote 13.

The Reactions of Sodium Pentafluorophenolate with Substituted Pentafluorobenzenes

RALPH J. DE PASQUALE AND CHRIST TAMBORSKI

Polymer Branch, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio

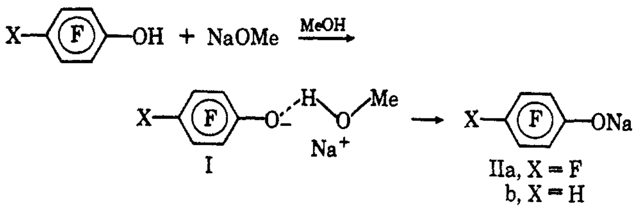
Received April 10, 1967

Sodium pentafluorophenolate was prepared by proton exchange using NaOMe–MeOH. This salt was freed from residual methanol and treated with a series of substituted pentafluorobenzenes (C_6F_5R, R = CF_3, CO_2Et, C_6F_5, Br, Cl, F, and H) using N,N-dimethylacetamide (DMAC) as solvent. The major product arising from displacement of fluorine *para* to the substituent was a fluorinated diphenyl ether. For some substituents (Cl, Br, and H), displacement of *o*-fluorine was competitive but minor. Mixtures of triphenyl ethers were occasionally observed. The relative reaction rates of these pentafluorobenzenes with sodium pentafluorophenoxide were measured in DMAC at 106°. These values when plotted against Hammett's substituent constant σ_p gave a reasonably straight line. From the slope, the σ_p of a pentafluorophenyl group can be estimated at +0.4. The halide ion mobilities were qualitatively measured as F > Cl or Br which is consistent with a two-step addition–elimination mechanism where the first step is rate determining.

In the past, the use of pentafluorophenoxide as a nucleophile has received limited attention.[1,2] Using aprotic conditions, we have found that this nucleophile reacts with a variety of substituted pentafluorobenzenes producing fair to excellent yields of the expected ethers.

Results[3a]

Reactions.—Pentafluorophenol and 4-hydrotetrafluorophenol were treated with cold NaOMe–MeOH. Removal of the solvent at reduced pressure left the salts as methanolates (I). Since the presence of alcohol would be detrimental to the salts' nucleophilic properties from both steric and electronic considerations, it was removed by heating in a vacuum oven. These salts were then treated with a series of substituted pentafluorobenzenes (see Table I).



SNAr reactions of charged anions with neutral substrates generally proceed faster in dipolar aprotic solvents than in protic solvents of similar dielectric constants.[3b] In our work dimethylformamide (DMF) and dimethylacetamide (DMAC) were used as the reaction media.

4-Bromononafluorodiphenyl ether (III) was the first of the series of fluorinated ethers prepared by the reaction between pentafluorophenolate and a substituted pentafluorobenzene. Experiments varying reaction parameters were carried out in order to obtain optimum yields of the desired ether (see Table II).

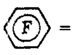
In DMF, incorporation of a solvent fragment into the perfluoroaromatic nucleus competed with the formation of III. The formation of this side product 4-N,N-dimethylaminobromotetrafluorobenzene (IV) was base catalyzed since it was produced faster and in higher yields in the presence of sodium pentafluorophenolate.

---

[1] W. J. Pummer and L. A. Wall, *J. Res. Natl. Bur. Std.*, **68A**, 277 (1964).

[2] E. S. Blake, G. A. Richardson, and J. A. Webster, Air Force Materials Laboratory Technical Report, RTD-TDR-63-4186.

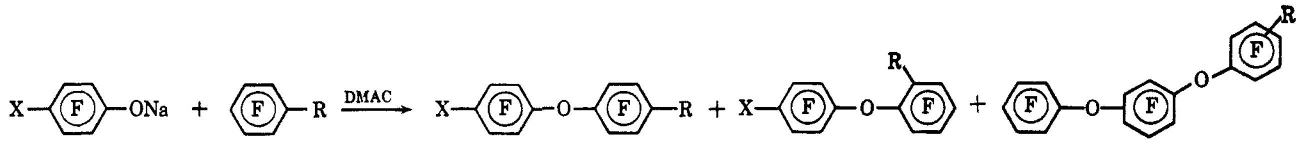
[3] (a) For purposes of clarity and economy of space, the following symbol is employed. Only the substituents other than fluorine are indicated.



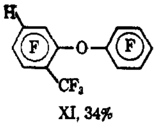
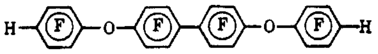
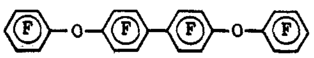
= C_6F_5

(b) R. A. Raphael, E. C. Taylor, and H. Wynberg, *Advan. Org. Chem.*, **5**, 9 (1965).

TABLE I
REACTION OF IIA AND IIB WITH RC_6F_5 IN DMAC



L M A B C

X	R	L:M	A, %	B, %[a]	C, %[a]	Other, %
F	Br	1:2	75 III	2	5	
F	Cl	1:2	68 VII	4	10	
F	F	1:4	40–60 VIII	. . .	8–11	
F	H	1:4	25 IX	5	5	
H	F	1:4	36	. . .	5	
F	CF_3	1:1.5	80 X	<1	<1	
F	CF_3[b]	1:1.5	. . .	. . .	. . .	 + isomers[a] and high-boiling products, 10% XI, 34%
F	CO_2Et	1:2	88 XII	1	1	
H	C_6H_5	1:3[b]	63 XIV	1	. . .	 XV, 1%
F	C_6H_5	2.5:1	2 XVI	1	. . .	 XVII, 90%

[a] Estimated by vpc. [b] Reactant is .

TABLE II
REACTIONS OF IIA WITH BROMOPENTAFLUOROBENZENE

Mole ratio, C_6F_5Br:C_6F_5ONa	Solvent	Temp, °C	Time, hr	% III	Side products	Comments
1:1	DMF	120	18	25[a]	IV (2%), HBP	Not to completion
1:1	DMF	145	20	Trace	IV (24%)	. . .
1:3	DMF	145	4.5	2[b]	Polymer	. . .
3:1	DMF	145	4.5	50[b]	(2%) IV	. . .
1:0	DMF	145	72	. . .	(10%) IV	Not to completion
1:1	HBE[c]	150	10	Trace	. . .	. . .
3:1	HBE[c]	150	10	Trace	. . .	. . .
1:1	DMAC	120	24	40[a]	HBP[d] (20%)	No IV
2:1	DMAC	110	8	75[a]	HBP[d] (5%)	No IV

[a] Isolated. [b] Estimated by vpc. [c] HBE = $CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2OCH_3$. [d] HBP = higher boiling products.

By changing the solvent to DMAC, IV is no longer detected. DMAC seems to be the solvent of choice for these reactions.

Two peaks consistently preceded and followed III on analyzing the crude reaction mixtures by vapor phase chromatography (vpc). The fact that these peaks were barely separable from III suggests their isomeric nature. Their area ratios were 3:97:<1 (DMAC) (110°). Tedious separation of the first peak by preparative vpc afforded a colorless viscous oil that was characterized as 2-bromononafluorodiphenyl ether from its infrared and F^{19} nuclear magnetic resonance (nmr) spectra. The assignment of the peak following III to 3-bromononafluorodiphenyl ether seems reasonable but speculative.

Isomeric triphenyl ethers were detected in the reactions involving weakly activated pentafluorobenzenes (R = Br, Cl, F, and H). As the reaction proceeds the concentration of the expected product (A, Table I) and unreacted pentafluorobenzene become comparable and subsequent reaction with polyfluorophenoxide ion is competitive. The triphenyl ethers were minimized by using a twofold (or more) excess of substituted pentafluorobenzene to polyfluorophenoxide ion and lower reaction temperatures.

In the preparation of 4-chlorononafluorodiphenyl ether (VII) analysis of the crude reaction mixture (vpc) revealed three peaks of similar retention times in 6:94:<1 ratio. This is consistent with the assignment of the first peak to 2-chlorononafluorodiphenyl ether (*ortho* substitution) since it is documented that chloropentafluorobenzene has a greater *ortho*/*para* ratio than bromopentafluorobenzene[4] in nucleophilic reactions.

The reaction of hydropentafluorobenzene with pentafluorophenoxide ion does not go to completion. It follows that substrates less reactive toward nucleophiles than hydropentafluorobenzene would not be expected to undergo pentafluorophenoxide substitution efficiently under our reaction conditions.

Hydrolysis of 4-carboethoxynonafluorodiphenyl ether (XII) in basic medium followed by acidification gave the corresponding acid XIII. Analysis of the acid by vpc (injection port 275°) revealed one peak

---

(4) J. Burdon, *Tetrahedron*, **21**, 3373 (1965).

with a retention time identical with IX. Apparently the acid undergoes facile thermal decarboxylation.

The reaction of decafluorobiphenyl with a stoichiometric amount of IIa or IIb invariably led to a mixture of mono and diperfluorophenoxybiphenyls. Excess IIa smoothly converted decafluorobiphenyl to a disubstituted product XVII, while IIb and excess decafluorobiphenyl gave a monosubstituted product XIV.

Hammett's substituent constant (σ_p H $\sim$ F) predicts that the reaction rates of IIa and IIb on the same substrate would be of similar orders of magnitude. Since trial experiments verified the prediction, one would expect that the reaction of IIa with decafluorobiphenyl to give XVI and of IIb with decafluorobiphenyl to give XV as the major products could be achieved by changing the stoichiometry of the reactants.

Stability of Sodium Pentafluorophenolate.—When sodium pentafluorophenolate was refluxed in DMAC (165°) for 19 hr, the bulk of it was recovered as the phenol (75%) after acidification. It seems reasonable, therefore, to assume that little, if any, of the salt polymerized during the reactions which afforded substituted nonafluorodiphenyl ethers.

Relative Rate Data.—The relative rates of reaction between six pairs of substituted pentafluorobenzenes and sodium pentafluorophenolate were measured (Table III). Over-all second-order kinetics were assumed, first order in substituted pentafluorobenzene and first order in sodium pentafluorophenolate, similar to the kinetics found[5,6] for the reaction of methoxide ion with substituted pentafluorobenzenes.

Table III

Relative Rates of Substituted Pentafluorobenzenes

1. $\dfrac{kC_6F_5CF_3}{kC_6F_5CO_2Et} = 8.2\ (106°)$

2. $\dfrac{kC_6F_5CO_2Et}{k(C_6F_5)_2} = 4.0$ (actual 2.0, 106°)

3. $\dfrac{kC_6F_5CO_2Et}{kC_6F_5Br} = 75\ (106°)$

4. $\dfrac{kC_6F_5Br}{kC_6F_5Cl} = 1.2\ (106°)$

5. $\dfrac{kC_6F_5Cl}{kC_6F_6} = 32$ (actual 5.4, 106°)

6. $\dfrac{kC_6F_6}{kC_6F_5H} = 0.91$ (actual 5.5, 106°)

C_6F_5X	Relative rate
CF_3	2.4×10^4
CO_2Et	2.9×10^3
C_6F_5	7.3×10^2
Br	39
Cl	32
H	1
F	0.91

The following expression was used to obtain the reported values where $[A]_1$ and $[C]_0$ refer to initial con-

$$K = \frac{\log \dfrac{[A]_0 - [B]}{[A]_0}}{\log \dfrac{[C]_0 - [D]}{[C]_0}} = \text{relative rate of reaction}$$

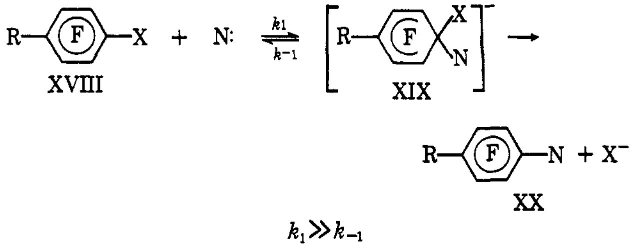
centrations of competing substituted pentafluorobenzenes and [B] and [D] refer to the concentrations of the 4-substituted nonafluorodiphenyl ethers produced.

The concentrations of B and D were measured by vpc using triphenylmethane as an internal standard. No allowance was made for the substitution of fluorine atoms *ortho* or *meta* to X since substitution of this type in our system is minor. In essence, therefore, the rates tabulated are the relative rates of formation of the *para* isomers.

Reactions 1–5 (Table III) were analyzed when they had proceeded from 25 to 90% completion. Reaction 6 was measured during its early stages (11–19%) to assure that aliquots were withdrawn before the hydropentafluorobenzene–pentafluorophenoxide reaction terminated (this reaction did not go to completion).

Discussion

In our pentafluorophenoxide-substituted pentafluorobenzene reactions *para* substitution predominated. With chloro- and bromopentafluorobenzenes as substrates the *ortho/para/meta* substitution ratios were 6:94: <1 and 3:97: <1, respectively. In these reactions, the *ortho/para* and the *meta/para* ratios are smaller than those obtained using methoxide ion as the nucleophile.[4,7] This is consistent with the intuitive expectation that the more reactive nucleophile (methoxide) should be less selective. A change, in nucleophile from methoxide to pentafluorophenoxide would also be expected to decrease the *ortho/para* ratio from steric considerations. The relative substitution rate at the *ortho* positions of chloro- and bromopentafluorobenzenes can be obtained from the observed isomer ratios and are 1.0 and 0.60, respectively. Their formation is approximately as fast as the formation of decafluorodiphenyl ether (VIII) formed in the hexafluorobenzene–sodium pentafluorophenolate reaction. Since VIII was not observed in the chloro- and bromopentafluorobenzene reactions, it follows that it is formed at a faster relative rate from hexafluorobenzene than from either chloro- or bromopentafluorobenzene. Furthermore, under the same reaction conditions bromopentafluorobenzene reacts considerably faster with pentafluorophenoxide ion than does *p*-dibromotetrafluorobenzene. The latter gives poor yields of III and does not go to completion.[8] Hence, the halide ion mobilities in these reactions are F < Cl or Br similar to the nitroaromatic systems previously reported.[9] This is consistent with a two-step addition–elimination mechanism where the formation of the intermediate XIX is rate determining.[10] The



$k_1 \gg k_{-1}$

N = nucleophile
R = substituent
X = halogen

---

[5] K. C. Ho and J. Miller, *Australian J. Chem.*, **19**, 423 (1966).

[6] J. Burdon, W. B. Hollyhead, C. R. Patrick, and K. V. Wilson, *J. Chem. Soc.*, 6375 (1965).

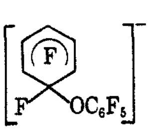
[7] L. A. Wall, W. J. Pummer, J. E. Fearn, and J. M. Antonucci, *J. Res. Natl. Bur. Std.*, **67A**, 481 (1963).

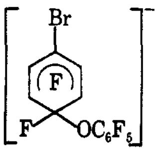
[8] R. J. De Pasquale and C. Tamborski, unpublished results.

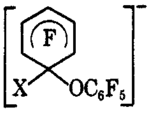
[9] C. W. L. Bevan, *J. Chem. Soc.*, 2340 (1951).

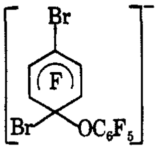
[10] J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 392.

transition state[11] leading to intermediate XXI and XXII is more easily attained than the ones corresponding to XXIII and XXIV, respectively.[12]


XXI


XXII

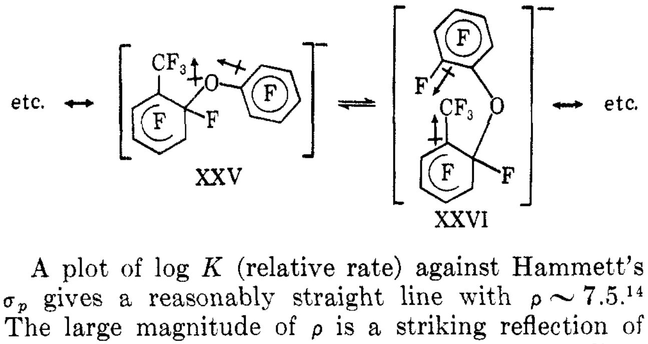

XXIII, X = Cl, Br


XXIV

It seems likely that very little, if any, carbon–halogen bond breaking is occurring in the rate-determining transition state. It is suggested that the substituted pentafluorobenzenes–sodium pentafluorophenolate reactions in our work follow this general mechanism.

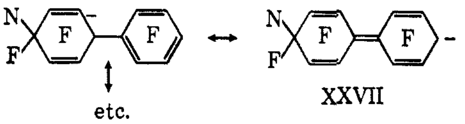
When CF_3, $CO_2C_2H_5$, and C_6F_5 were substitutents greater than 98% *para* substitution was observed. A pentafluorophenyl or carboethoxy group can afford a considerable amount of steric interaction to a nucleophile approaching the *ortho* sites. It is not surprising that these positions are unreactive.

The difference of reactivity between the *ortho* and *para* positions of octafluorotoluene can be qualitatively estimated by comparing the reactions of sodium pentafluorophenolate with 4-hydroheptafluorotoluene and octafluorotoluene. As expected the former reaction underwent substitution *ortho* to the CF_3 group affording XI and was very slow (approximately as fast as the C_6F_6 reaction). This reactivity difference between the *ortho* and *para* positions of octafluorotoluene is too large to ascribe to steric factors alone. Our rationale is that unfavorable dipole interactions between the fluorine atoms of the CF_3 group[13] and the pentafluorophenoxide substituent could raise the transition-state energy considerably (XXV and XXVI).



A plot of log K (relative rate) against Hammett's σ_p gives a reasonably straight line with $\rho \sim 7.5$.[14] The large magnitude of ρ is a striking reflection of the delocalization demanded by the intermediate carbanions.

From the graph the σ_p of a pentafluorophenyl group can be estimated at about +0.4. Decafluorobiphenyl is then expected to be more reactive toward nucleophiles than hexafluorobenzene or 2,3,4,5,6-pentafluorobiphenyl. Apparently, a pentafluorophenyl group stabilizes an anionic intermediate appreciably. The azimuthal angle between the rings of decafluorobiphenyl in solution has been estimated at 50° by nmr.[15] Therefore, this stabilization is probably a combination of inductive and resonance effects with the former predominating. Contribution of XXVII, to the overall resonance hybrid of an intermediate is limited since



unfavorable dipole–dipole interactions of *o*-fluorines restrict ring coplanarity and decrease orbital overlap between the perfluorophenyl rings.

Experimental Section

The fluoroaromatics in this work were purchased from Imperial Smelting (N.S.C.) Ltd., Avonmouth, England, and were used without further purification. The DMAC was analytical grade and dried over molecular sieve 5A prior to use; all other solvents utilized were analytical grade.

Melting points were determined in an oil-bath apparatus. Boiling points and melting points are uncorrected. The F^{19} nmr spectra were recorded on a Varian V-4300-2-DP spectrometer at 40 Mc/sec. Chemical shifts are reported in parts per million from external trifluoracetic acid (TFAA). Carbon tetrachloride was used as the solvent unless otherwise stated. The H^1 nmr spectra were recorded on a Varian A-60 spectrometer in carbon tetrachloride. Chemical shifts are reported as parts per million from the internal standard tetramethylsilane (TMS). Infrared spectra were run on a Perkin-Elmer Infracord spectrophotometer as KBr pellets or as liquid films. Vapor phase chromatography analysis was done on a F & M Model 500 instrument using a helium flow of 60 cc/min, 6 ft × 0.25 in. column, 20% Apiezon L on 60–80 mesh Chromosorb W, and programmed from 100 to 275° (21°/min) after which it was held at this temperature. The mass spectra were recorded on an AEI MS-9 mass spectrometer.

Sodium 4-Hydrotetrafluorophenolate (IIb).—Under nitrogen, 4-hydrotetrafluorophenol (83.0 g, 0.500 mole) dissolved in 100 ml of methanol was added dropwise with stirring over a 1-hr period to 700 ml of a 0.714 N NaOMe–MeOH solution. The temperature was maintained at −10 to 0°. At the completion of the addition, an aspirator was attached to the system and the methanol was removed at reduced pressure (*ca*, 20 mm). The white solid that remained was triturated with 300 ml of chloroform and dried in a vacuum oven (70° at 1 mm) leaving the salt, melting point over 350° (yield 98–100%).

Sodium Pentafluorophenolate (IIa).—The procedure for the preparation of sodium 4-hydropentafluorophenolate was followed. A white powdery salt, mp 320 dec, was obtained in a 95–100% yield.

General Procedure.—The two reactants, sodium pentafluorophenolate and substituted pentafluorobenzene, were added to DMAC and stirred under nitrogen. The solution was heated to *ca.* 110° and remained at this temperature until the product peak (vpc) no longer increased. The solution was added to about three times its volume of distilled H_2O. The bottom layer was separated and taken up in petroleum ether (bp 30–60°). The resultant solution was extracted with water (the water extracts were discarded) and concentrated (rotary evaporator) leaving the bulk of the product and unreacted substituted pentafluorobenzene (fraction I). The original aqueous DMAC solution was then extracted with petroleum ether. These combined extracts were further extracted with water,

---

(11) In these reactions the transition states are expected to resemble their corresponding intermediates. For ease of representation when the diagram of a transition state is called for its related intermediate will be substituted.

(12) This assumes that the difference in the reaction rates of the halopentafluorobenzenes corresponds to the energy of the transition states. This is reasonable if one assumes that the ground-state energies and frequency factors of the halopentafluorobenzenes are of the same orders of magnitude. (see ref 4–6).

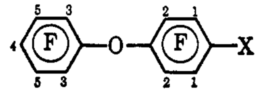
(13) It is worthy to note that the nmr spectrum of XI shows that these atoms are coupled to the *ortho* fluorine atoms of the fluorophenoxy substituent by 4 cps, which suggests their spatial proximity.

(14) If σ^- values were available, ρ would be *ca.* 5–6.

(15) N. Boden, J. W. Emsley, J. Feeney, and L. H. Sutchliffe, *Mol. Phys.*, **8**, 467 (1964).

Table IV

Nuclear Magnetic Resonance



X	Chemical shift of fluorines, ppm (multiplicities)[a]				
	1	2	3	4	5
CN	53.2 (m)	75.0 (m)	76.8 (bd)	78.6 (dt)	82.0 (dtf)
CF_3	62.3 (m)	78.5 (m)	78.5 (m)	81.0 (dt)	84.2 (dtf)
	CF_3(−23.3, triplet)				
CO_2Et	61.0 (m)	78.3 (m)	78.3 (m)	81.0 (dt)	83.3 (dtf)
Br	54.8 (m)	78.1 (m)	79.0 (bd)	82.0 (dt)	84.5 (dtf)
Cl	61.7 (m)	78.0 (m)	78.0 (bd)	80.9 (dt)	83.5 (dtf)
F	...	...	78.4 (bd)	81.1 (dt)	83.7 (dtf)
H	59.5 (m)	78.3 (bd)	78.3 (bd)	80.7 (dt)	83.2 (dtf)
C_6F_5O–C_6F_5	58.9 (m)	77.5 (m)	77.5 (m)	80.3 (dt)	85.0 (dtf)

[a] m = multiplet; bd = broad doublet; dt = distorted triplet; dtf = distorted triplet with fine structure.

dried ($MgSO_4$), and concentrated on a rotary evaporator (fraction II). Fractions I and II were combined and distilled at reduced pressure (*ca.* 10 mm) until the removal of the substituted pentafluorobenzene had been effected. The pot residue solidified on cooling to give a crude yield of product. This material was dissolved in petroleum ether and eluted from neutral alumina (activity I) with petroleum ether. On concentrating the petroleum ether solution an analytical sample was obtained. For some cases, recrystallization from methanol was necessary to remove isomeric materials.

4-Bromonoafluorodiphenyl Ether (III).—Bromopentafluorobenzene (8.4 g, 0.034 mole), sodium pentafluorophenolate (3.5 g, 0.017 mole), and 100 ml of DMAC were heated at 110° for *ca.* 9 hr and worked-up according to the general procedure. There was obtained 5.7 g of crude product (70%), mp 79–82° (95–98% III by vpc). This material was purified by column chromatography followed by recrystallization from MeOH to give an analytical sample, mp 85–86°.

Anal. Calcd for $C_{12}F_9BrO$: C, 35.06; Br, 19.44; F, 41.66. Found: C, 34.98; Br, 19.25; F, 41.67.

Analysis (vpc) of the crude product revealed the presence of three peaks in a 3:97:<1 ratio. Tedious separation of the first peak by preparative vpc afforded a colorless viscous oil, subsequently characterized as 2-bromononafluorodiphenyl ether (V). Its infrared spectrum was similar to III. Its F^{19} nmr spectrum displayed absorptions at 79.3 (area 2), 83.0 (area 1), and 84.9 ppm (area 2) whose multiplets were characteristic of a pentafluorophenoxy group. The remaining multiplets resonated at 52.7 (doublet with fine structure, area 1, F_3-fluorine at ring position 3), 77.2 (broad doublet, area 2, F_5 and F_6), and 80.4 ppm (multiplet, area 1, F_4). By irradiating the 77.2-ppm doublet, the absorption at 52.7 ppm resolved into a sharp doublet ($J \sim 21$ cps).

4-Chlorononafluorodiphenyl Ether (VII).—Sodium pentafluorophenolate (10.4 g, 0.052 mole), chloropentafluorobenzene (21.2 g, 0.104 mole), and 300 ml of DMAC were stirred and heated to 110° for *ca.* 15 hr. After the usual work-up, 12.7 g (68%) of product was isolated, mp 65–69° consisting of a 6:94 ratio of two isomers (vpc). It was further purified by alumina chromatography and recrystallization from methanol to yield a pure product, mp 74–75°.

Anal. Calcd for $C_{12}F_9ClO$: C, 39.32; Cl, 9.67; F, 46.65. Found: C, 39.54; Cl, 9.90; F, 46.45.

The F^{19} nmr data is presented in Table IV.

Decafluorodiphenyl Ether (VIII).—Sodium pentafluorophenolate (55.1 g, 0.250 mole), hexafluorobenzene (176 g, 1.00 mole), and 700 ml of DMAC were stirred and heated to 110° for approximately 24 hr. The usual work-up afforded 59.1 g of crude product, mp 54–59° (85% purity), which corresponds to a 59% yield. Sublimation of the crude product (65–70° at 0.2 mm) afforded decafluorodiphenyl ether, mp 70–73° (lit.[2] mp 72°). The residue was further sublimed (130° at 0.2 mm) and gave a mixture of perfluoroterphenyl ethers (8–11%), mp 142–150°.

4-Hydrononafluorodiphenyl Ether (IX). Method A.—Sodium pentafluorophenolate (3.5 g, 0.017 mole), pentafluorobenzene (11.4 g, 0.068 mole), and 100 ml of DMAC were heated to 110° and maintained at that temperature for 2 days. The usual work-up gave a crude product that was purified by sublimation to obtain 1.41 g (25%) of a white crystalline solid, mp 54–55°.

Method B.—In 150 ml of DMAC, sodium 4-hydropentafluorophenolate (7.0 g, 0.037 mole) and hexafluorobenzene (25.2 g, 0.136 mole) were stirred and heated to 110° for 24 hr. After the usual work-up, the solid isolated was triturated with petroleum ether and filtered. The insoluble material (0.6 g, mp 138–142°) was 85% one component (vpc, probably a terphenyl ether). The filtrate was eluted from a short alumina column with petroleum ether and after evaporation of the solvent deposited 4.4 g (36%) of an analytical sample, mp 54–56°.

Anal. Calcd for $C_{12}HF_9O$: C, 43.39; H, 0.30; F, 51.49. Found: C, 43.35; H, 0.33; F, 51.58.

The H^1 nmr spectrum exhibited a triplet of triplets centered at 7.0 ppm with *o*-fluorine–hydrogen and *m*-fluorine–hydrogen coupling constants of 10 and 6.7 cps, respectively. For F^{19} nmr see Table IV.

4-Trifluoromethylnonafluorodiphenyl Ether (X).—Octafluorotoluene (5.15 g, 0.0218 mole) and sodium pentafluorophenolate (3.00 g, 0.0145 mole) were stirred and heated in 150 ml of DMAC for 1.5 hr at 100°. Following the general isolation procedure, 4.6 g (80%) of product was isolated, mp 61–63°. Purification *via* alumina chromatography gave an analytical sample, mp 62–63°.

Anal. Calcd for $C_{13}F_{12}O$: C, 39.02; F, 56.98. Found: C, 39.15; F, 56.32.

The F^{19} nmr data is presented in Table IV.

2-Trifluoromethyl-5-hydrooctafluorodiphenyl Ether (XI).—4-Hydroheptafluorotoluene (10.0 g, 0.0485 mole) and sodium pentafluorophenolate (12.6 g, 0.0582 mole) were heated in 250 ml of DMAC at 110° for 2 weeks. Following the general procedure, 9.4 g of a dark oil was isolated and eluted from alumina to give 8.0 g of a colorless liquid that was 80% XI (vpc, 34%). This material was distilled to obtain XI (of 96% purity by vpc), bp 96° (1 mm). The high-resolution mass spectrum supports the formula $C_{13}HF_{11}O$ (Calcd: 381.9851. Found: 381.9827 (parent ion).), with a fragment ion peak $C_{13}HF_{10}O$ (Calcd: 362.9868. Found: 362.9867.). The H^1 nmr consisted of a first order triplet of doublets centered at 7.4 ppm ($J_{F_{ortho}H} = 10$ cps and $J_{F_{meta}H} = 7$ cps). Its F^{19} nmr spectrum was consistent with the assigned structure.

4-Carboethoxynonafluorodiphenyl Ether (XII).—Sodium pentafluorophenolate (16.4 g, 0.052 mole), ethylpentafluorobenzoate (33.6 g, 0.104 mole), and 300 ml of DMAC were heated to 110° and maintained at that temperature for 2–3 hr. After the usual work-up 18.4 g (88%) of product mp 45–46° was isolated. Alumina chromatography yielded an analytical sample, mp 46–47°.

Anal. Calcd for $C_{15}H_5F_9O$: C, 44.57; H, 1.25; F, 42.31. Found: C, 44.68; H, 1.30; F, 41.87.

The H^1 nmr spectrum of this ester exhibited a quartet at 4.45 ppm (area 2) and a triplet at 1.42 ppm (area 3, $J = 7$ cps). The F^{19} nmr data is presented in Table IV.

4-Nonafluorodiphenyl Ether Carboxylic Acid (XIII).—Sodium hydroxide (0.90 g, 0.025 mole) dissolved in 20 ml of water was added to 4-carboethoxynonafluorodiphenyl ether (4.4 g, 0.011 mole) dissolved in 100 ml of tetrahydrofuran (THF). The mixture was stirred at room temperature for *ca.* 72 hr. After evaporation of the solvent, 50 ml of water was added, and the solution was filtered. The sodium salt of the acid was dried in a vacuum oven and weighed 3.3 g (76%), mp 305–308° dec. The above aqueous filtrate was acidified (HCl) and extracted with ether (three 30-ml portions). The combined extracts were dried ($MgSO_4$) and concentrated depositing a pinkish white solid. Two recrystallizations from petroleum ether (bp 90–120°) gave 0.43 g (10.5%) of an analytical sample, mp 168–169°.

Anal. Calcd for $C_{13}HF_9O_3$: C, 41.51; H, 0.27; F, 45.46. Found: C, 41.23; H, 0.36; F, 45.74.

The sodium salt was quantitatively converted to the acid by dissolving it in hot water, adding concentrated HCl, filtering, and drying.

4-(4-Hydrotetrafluorophenoxy)nonafluorobiphenyl (XIV).—Decafluorobiphenyl (155 g, 0.411 mole), was dissolved in 500 ml of DMAC under nitrogen. To this stirred solution sodium 4-hydrotetrafluorophenolate (25.8 g, 0.137 mole) was added, reaction mixture was heated to 100° and maintained at this temperature for 15 hr. A sample of the mixture was withdrawn and analyzes by vpc indicated two peaks (besides solvent), decafluorobiphenyl, and the desired product. There was also a trace (~2%) of a higher boiling component which was identified as a disubstituted biphenyl. The cooled mixture was added to 1500 ml of distilled water and the solid that settled was filtered, dried, and fractionally sublimed (30° at 0.5 mm). The first sublimate consisted of *ca.* 90% decafluorobiphenyl and 10% of the desired product XIV. The residue from the first sublimation was placed in a flask and heated at reduced pressure (100° at 0.3 mm) to remove the last traces of decafluorobiphenyl. On cooling the residue, 32.0 g of an off-white solid, mp 58–60°, was obtained. A white sample, mp 61–63°, was obtained by eluting a petroleum ether (30–60°) solution of the residue from an alumina column with petroleum ether.

From the first sublimate (90:10 mixture), an additional 9.6 g of XIV (98% pure) was obtained by recrystallization from methanol (to remove the decafluorobiphenyl) and further sublimation. The over-all yield of XIV was 63%.

Anal. Calcd for $C_{18}HF_{13}O$: C, 45.00; H, 0.21. Found: C, 44.93; H, 0.26.

The H^1 nmr spectrum of this compound exhibited a triplet of triplets centered at 7.0 ppm with *o*-fluorine–hydrogen and *m*-fluorine–hydrogen coupling constants of 9.8 and 7.0 cps, respectively.

In a preliminary experiment equimolar amounts of decafluorobiphenyl and sodium 4-hydrotetrafluorophenolate under similar reaction conditions gave rise to a mixture of mono- and disubstituted perfluorobiphenyls XIV and XV, respectively.

Separation was achieved by careful alumina chromatography; the disubstituted perfluorobiphenyl (XV) had mp 106–108°.

Anal. Calcd for $C_{24}H_2F_{16}O_2$: C, 46.00; H, 0.32; mol wt, 626. Found: C, 46.03; H, 0.49; mol wt 626 (mass spectrum).

4,4′-Bis(pentafluorophenoxy)octafluorobiphenyl (XVII).—Sodium pentafluorophenolate (25.88 g, 0.125 mole) and decafluorobiphenyl (16.7 g, 0.050 mole) were added to 600 ml of DMAC in a nitrogen atmosphere, stirred, and heated between 80 and 90° for 140 hr. The cooled reaction mixture was added to 1500 ml of water and the tan (crude) product that settled was filtered and dried (27.5 g), mp 161–165°. The aqueous DMAC solution was extracted with chloroform (three 100-ml portions) and the chloroform extracts were extracted with water (three 100-ml portions), dried ($MgSO_4$), and evaporated to dryness. The dark residue that remained was triturated with cold methanol and filtered leaving 3.5 g of a tan solid, mp 160–165°. The combined crude products weighed 31.0 g (90.5%). This crude material was dissolved in methylene chloride and eluted from alumina with methylene chloride followed by recrystallization from ethanol–benzene to give an analytical sample, mp 170–171°.

Anal. Calcd for $C_{24}F_{18}O_2$: C, 43.53; F, 51.64. Found: C, 43.44; F, 51.75.

For the F^{19} nmr XVII see Table IV.

A trial experiment gave a mixture of mono- and disubstituted pentafluorophenoxyperfluorobiphenyls. The monosubstituted isomer XVI, mp 57–59°, was isolated and characterized. Its molecular weight was 498 (mass spectrum) (calcd for XVI, 498) and its F^{19} nmr spectrum was consistent with the assigned structure.

The Polymerization of Sodium Pentafluorophenolate.—Sodium pentafluorophenolate (10.0 g, 0.0498 mole) was refluxed in 100 ml of DMAC for 19 hr in a nitrogen atmosphere. After the usual work-up 1.4 g of a brittle dark polymer (completely molten at 180°) and 8.0 g (90% pure, vpc) of pentafluorophenol (obtained after acidification) were the only isolable products.

Relative Rate Data

The relative rates of reaction between six pairs of monosubstituted pentafluorobenzenes were measured and correlated. The stoichiometry utilized in each experiment is listed in Table V.

Table V

Stoichiometry of Relative Rate Reactions[a]

Expt	$C_6F_5X_1$	X_1 equiv	$C_6F_5X_2$	X_2 equiv
1	CF_3	0.0256	CO_2Et	0.0527
2	CO_2Et	0.0255	C_6F_5	0.0680
3	CO_2Et	0.0255	Br	0.0680
4	Br	0.0425	Cl	0.0850
5	Cl	0.0510	F	0.0850
6	F	0.0340	H	0.0680

[a] In all of these reactions 0.0170 equiv of C_6F_5ONa was used in 60.0 ml of DMAC at 106°.

The reaction vessel was purged with nitrogen and immersed in an oil bath. The solvent and the two substituted pentafluorobenzenes were added and allowed to attain constant temperature. To the stirred solution, sodium pentafluorophenolate was introduced. Aliquots (1.0 ml) were periodically withdrawn, added to a standard, and analyzed by vpc. From the areas of the two substituted diphenyl ethers (standardized with triphenylmethane) the relative rates were calculated.

For each experiment three to five aliquots were withdrawn at different reaction times, and a relative rate was calculated for each aliquot (there was no more than a 5% deviation). The average relative rate was recorded.

The aliquots from each experiment were quenched by allowing them to cool to room temperature with the exception of experiment one (Table V) which was quenched in Dry Ice–acetone. Chemical quenching seemed unnecessary since a freshly prepared solution of octafluorotoluene (the most reactive) and sodium pentafluorophenolate in DMAC showed no trace of product when analyzed by vpc.

Registry No.—IIa, 2263-53-8; IIb, 14055-43-7; III, 14055-44-8; V, 14055-45-9; VII, 14055-46-0; VIII, 1800-30-2; IX, 14055-48-2; X, 14055-49-3; XI, 14055-50-6; XII, 14055-51-7, XIII, 14055-52-8; XIV, 14055-53-9; XV, 14055-54-0; XVI, 14055-55-1; XVII, 14055-56-2.

Acknowledgments.—The authors wish to thank J. V. Pustinger, Jr., and J. Strobel of Monsanto Research Corp. for obtaining the F^{19} nmr spectra and R. E. Rhodes of Mellon Institute for obtaining the mass spectra reported in this work.