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SHORT COMMUNICATION

THE SYNTHESIS OF PERFLUORO(ALKYLETHERPHENYL) PHOSPHINES

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The first perfluorophenyl substituted phosphine, $(C_6F_5)_3P$ was prepared by Wall et al. [1]. Since then numerous pentafluorophenylphosphorous compounds [2] have been prepared and their properties studied. Substituted perfluorophenylphosphines $(R_fC_6F_4)_3P$ however have not been extensively studied. Those that have been reported are all solids: $(C_6F_5)_3P$, m.p. 116° [1]; $(p\text{-}CF_3C_6F_4)_3P$, m.p. 103-105° [3]; $(p\text{-}C_8F_{17}C_6F_4)_3P$, m.p. 117° [3]; and $(p\text{-}C_6F_5OC_6F_4)_3P$, m.p. 135-137° [4].

One of our objectives was to synthesize perfluoroarylphosphine compounds that are liquid at ambient temperature. Since it appeared that perfluoroalkyl substituents on the perfluorophenyl group did not decrease the melting point of the $(C_6F_5)_3P$ sufficiently, other substituent groups were sought. This study was therefore directed at the synthesis of perfluoro-

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alkylether ($R_f'OR_f$ will be referred to as any mono or poly oxygen containing perfluoroalkylether group) substituted phenyl phosphines $(R_f'OR_fC_6F_4)_3P$.

Perfluoroarylphosphines have been conveniently synthesized through organometallic intermediates [1,2].

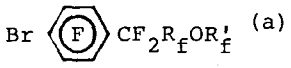
$$3C_6F_5M + PCl_3 \longrightarrow (C_6F_5)_3P + 3MCl$$
$$M = MgX,\ Li$$

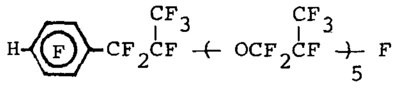
After examining numerous other procedures, the following sequence was adopted.

$$p\text{-}BrC_6F_4Br + C_2H_5MgBr \longrightarrow C_2H_5Br + p\text{-}BrC_6F_4MgBr$$
$$p\text{-}BrC_6F_4MgBr + CuX \longrightarrow MgBrX + p\text{-}BrC_6F_4Cu$$
$$p\text{-}BrC_6F_4Cu + R_f'OR_fC(O)F \longrightarrow CuF + p\text{-}BrC_6F_4C(O)R_fOR_f'$$
$$p\text{-}BrC_6F_4C(O)R_fOR_f' + SF_4/HF \longrightarrow p\text{-}BrC_6F_4CF_2R_fOR_f'$$
$$p\text{-}BrC_6F_4CF_2R_fOR_f' + C_4H_9Li \longrightarrow C_4H_9Br + p\text{-}LiC_6F_4CF_2R_fOR_f'$$
$$3p\text{-}LiC_6F_4CF_2R_fOR_f' + PCl_3 \longrightarrow 3LiCl + (p\text{-}R_f'OR_fCF_2C_6F_4)_3P$$

The ketone intermediate $p\text{-}BrC_6F_4C(O)R_fOR_f'$ cannot be synthesized from the organolithium or Grignard intermediate since on reaction with the acid fluoride $R_fOR_fC(O)F$ the para bis ketone $R_f'OR_fC(O)C_6F_4C(O)R_fOR_f'$ is produced [5]. The organocopper compound however reacts readily with the acid fluoride to produce only the mono ketone $p\text{-}BrC_6F_4C(O)R_fOR_f'$ in high yields [5,6,7]. Both primary $(R_fOR_fCF_2C(O)F)$ and secondary $(R_f'OR_fCF(CF_3)C(O)F)$ acid fluorides react readily with the organocopper intermediate. The reaction between the $p\text{-}BrC_6F_4C(O)R_fOR_f'$ and SF_4/HF [8] produced high yields of fluorinated product $p\text{-}BrC_6F_4CF_2R_fOR_f'$ (see Table I). The above sequence of reactions, although

TABLE I


(a)

$R_f'OR_f$-	% Yield	B.P. °C/mm	M.S.	Elemental Analysis Calc'd/Found	
				C	Br
$CF(CF_3)OC_3F_7$	80.5	109/55	562-564 $(M)^+$	$\frac{25.6}{25.5}$	$\frac{14.2}{14.3}$
$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$	68	76/2	728-730 $(M)^+$	$\frac{24.7}{24.8}$	$\frac{10.9}{10.5}$
$CF(CF_3)[OCF_2CF(CF_3)]_4OC_3F_7$	74	122/0.01	1226-1228 $(M)^+$	$\frac{23.4}{23.4}$	$\frac{6.5}{6.5}$
$CF_2(OC_2F_4)_2OC_2F_5$	81	115/10	694-696 $(M)^+$	$\frac{24.1}{24.1}$	$\frac{11.5}{11.5}$
$CF_2(OCF_2)_3OCF_3$	68	117/30	610-612 $(M)^+$	$\frac{23.5}{23.1}$	$\frac{13.0}{13.0}$
	81	98/0.016	1148 $(M)^+$	$\frac{25.1}{24.9}$	$H=\frac{0.09}{0.13}$

(a) All new compounds

seemingly long, can be readily adopted to prepare numerous R_f or $R_f'OR_f$ substituted aromatic compounds. Since other isomeric bromofluoroarylcopper compounds can be prepared it is likely that any variety of $BrAr_fR_fOR_f'$ or $BrAr_fR_f$ compounds may be prepared by this method.

The $p\text{-}LiC_6F_4CF_2R_fOR_f'$ organometallic compounds behave as typical perfluoroaryllithium intermediates. They are temperature sensitive, hydrolyze easily to $p\text{-}HC_6F_4CF_2R_fOR_f'$ and react with metallic or metalloidal halides. For example with PCl_3 the tris substituted product $(R_f'OR_fCF_2C_6F_4)_3P$ can be prepared readily while with $(C_6H_5)_2PCl$, $(C_6H_5)_2PC_6F_4CF_2R_fOR_f'\text{-}p$ is produced (see Table II). Similarly with $SnCl_4$ the tetra substituted product is produced.

$$4P\text{-}R_f'OR_fCF_2C_6F_4Li + SnCl_4 \longrightarrow 4LiCl + (p\text{-}R_f'OR_fCF_2C_6F_4)_4Sn$$

Substitution of the perfluorophenyl group by an $R_f'OR_f$ group has a dramatic effect on lowering the melting point. In all examples studied viscous liquids (at room temperature) were obtained. The $(R_f'OR_fC_6F_4)_3P$ compounds are soluble in fluorinated solvents, have low volatility, and are resistant to oxidation, much like the $(C_6F_5)_3P$ [1].

These phosphines have an unusual property of behaving as anticorrosion agents for poly(perfluoropropyleneoxide) fluids exposed to various metals in an oxidative high temperature environment [9].

EXPERIMENTAL

General Comments

Reactions involving organometallic reagents were carried out under dry nitrogen with usual precautions for rigorous exclusion of moisture and air. Tetrahydrofuran was dried by refluxing over metallic sodium followed by distillation from calcium hydride prior to use. Anhydrous diethyl ether (Mallinckrodt) was used without further purification. All new compounds were characterized by NMR (^{19}F and ^{1}H), IR, mass spectral and combustion analysis. The GC analysis were performed on an F&M Model 700 instrument using 6 ft., 10% SE-30 on Chromosorb W column. Mass spectral analysis were performed using an electron impact mass spectrometer (CEC-21-110B). The following examples described the general procedure for the synthesis of the perfluoroketones [5], fluorination via SF_4/HF and the synthesis of the phosphines via the organolithium intermediates.

Synthesis of p-$BrC_6F_4C(O)CF(CF_3)OCF_2CF(CF_3)OC_3F_7$

To a solution of 1,4-dibromotetrafluorobenzene (30.8 g, 0.100 moles) in anhydrous tetrahydrofuran (250 ml) at 0°, ethylmagnesium bromide (61.7 ml of a 1.62 M diethyl ether solution) was slowly added. After the solution was stirred for approximately 0.5 h at 0°, cuprous chloride (12.5 g, 0.125 mole) was added. Stirring was continued while the reaction mixture was allowed to rise to room temperature. To this organocopper intermediate cooled to 0°, the perfluoroacyl fluoride [where $R_f'OR_f = C_3F_7OCF(CF_3)CF_2OCF(CF_3)$] (49.8 g, 0.100 mole) was slowly added. The reaction mixture was stirred at room temperature for 15 h. The resulting brown mixture was hydrolyzed with 2N. HCl (100 ml). The mixture was extracted three times with diethyl ether (600 ml total). The diethyl ether layer was phase separated and dried ($MgSO_4$). Distillation yielded the ketone [5], b.p. 248°-251° yield 65.5%.

Synthesis of $p\text{-}BrC_6F_4CF_2CF(CF_3)OCF_2CF(CF_3)OC_3F_7$

The above ketone (34.7 g, 0.0514 mole) was placed into 300 ml Monel pressure vessel. The vessel was cooled in a Dry Ice bath while anhydrous hydrogen fluoride (9.2 g, 0.46 mole) and sulfur tetrafluoride (24.8 g, 0.23 mole) were added. The pressure vessel was sealed, rocked and heated to 180° for 18 h. The vessel was cooled, vented and the contents were washed with diethyl ether. The solvent was evaporated and the residue was fractionally distilled to yield the fluorinated product (see Table I), b.p. 76°/2. mm, in 68% yield. Nuclear magnetic resonance and infrared analysis were consistent with the proposed structure.

Synthesis of $(C_6H_5)_2P[p\text{-}C_6F_4CF_2CF(CF_3)OCF_2CF(CF_3)OC_3F_7]$

To a solution of $p\text{-}BrC_6F_4CF_2CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ (24.5 g, 0.02 moles) in anhydrous tetrahydrofuran (175 ml) and anhydrous diethyl ether (100 ml) at -78° n-butyllithium (15.4 ml. of 1.3 M hexane solution, 0.020 mole) was added. After approximately 1 h a diethyl ether (100 ml) solution of diphenylchlorophosphine (4.25 g, 0.019 mole) was added at -78°. The reaction was stirred at this temperature for approximately 15 h allowed to reach room temperature and stirred for an additional 15 h. The reac-

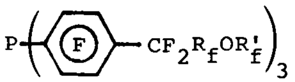
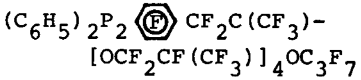
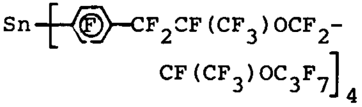

(a)

TABLE II

$R_f'OR_f$-	% Yield	B.P.°C/mm	M.W. Calc'd/Found	Elemental Analysis Calc'd/Found	
				C	P
$CF(CF_3)OC_3F_7$	78	189/0.01	$\frac{1480}{1480}$	$\frac{29.2}{29.2}$	$\frac{2.09}{2.03}$
$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$	70	201/0.005	$\frac{1978}{1978}$	$\frac{27.3}{27.3}$	$\frac{1.57}{1.34}$
$CF(CF_3)[OCF_2CF(CF_3)]_4OC_3F_7$	30	178/0.003	$\frac{3472}{(b)}$	$\frac{24.9}{24.8}$	$\frac{0.89}{1.01}$
$CF_2(OC_2F_4)_2OC_2F_5$	69	157/0.005	$\frac{1876}{(b)}$	$\frac{26.8}{26.7}$	$\frac{1.65}{1.60}$
$CF_2(OCF_2)_3OCF_3$	59	157/0.005	$\frac{1624}{1624}$	$\frac{26.6}{26.6}$	$\frac{1.91}{1.52}$
	50	148/0.005	$\frac{1332}{1332}$	$\frac{32.5}{32.2}$	$H=\frac{0.76}{0.85}$
	52	222/0.01	$\frac{2715}{2716}$ (120Sn)	$\frac{26.5}{26.8}$	$Sn=\frac{4.37}{3.74}$

(a) All new compounds, (b) Not determined tion was hydrolyzed with 6 N hydrochloric acid, phase separated, dried and distilled under reduced pressure to yield a viscous liquid product (see Table II), b.p. 148°/0.005 mm in approximately 50% yield. Nuclear magnetic resonance and infrared analysis were consistent with the structure.

The other triperfluoroarylphosphines were synthesized by the above procedure except PCl_3 was used. The tetraperfluorophenyltin compound was prepared from $SnCl_4$ (see Table II).

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