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SYNTHESIS OF PENTAFLUOROPHENYL ESTERS FROM ACID FLUORIDES AND POTASSIUM PENTAFLUOROPHENOXIDE

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SUMMARY

The reaction of potassium pentafluorophenoxide with acid fluorides has been investigated and found to yield pentafluorophenyl esters. The compounds $CH_3C(O)OC_6F_5$, $CF_3C(O)OC_6F_5$, $CF(O)OC_6F_5$, $CF_3OOC(O)OC_6F_5$, and $(C_6F_5O)_2CO$ have been prepared. Physical and spectral data for each compound are reported.

INTRODUCTION

While many pentafluorophenyl esters of the type $C_6F_5C(O)OR$ have been prepared, few derivatives with the C_6F_5 group in the ester portion of the molecule have been synthesized [1]. Recently the preparation of perfluoro-t-butyl esters by the reaction of KOC_4F_9 with acid fluorides has been reported [2]. We wish to report the extension of this reaction type to the formation of pentafluorophenyl esters from KOC_6F_5 and acid fluorides (1). This reaction

$$KOC_6F_5 + XC(O)F \quad KF + XC(O)OC_6F_5 \tag{1}$$

provides a convenient method for the synthesis of new compounds of the type $XC(O)OC_6F_5$ ($X = CH_3$, CF_3, CF_3OO, C_6F_5O). The preparation of the compounds $CH_3C(O)OC_6F_5$ and $CF_3C(O)OC_6F_5$ have been briefly reported previous to this work [1]. The compound, $CF_3OOC(O)OC_6F_5$, is the third example of a pentafluorophenyl derivative containing a peroxide linkage ($C_6F_5OOC_6F_5$ and $C_6F_5C(O)OOC(O)C_6F_5$ are known) [3].

EXPERIMENTAL

General

Standard high vacuum techniques were used throughout. Quantities of reactants and products were measured either by direct weighing or by the relationship n = PV/RT with pressures measured on a Wallace and Tierman Model FA 145 differential pressure gauge. Molecular weights were determined by the vapor density method. Vapor pressure data were obtained by a static method and the data analysed by a computer assisted least squares fit to both linear and quadratic equations with the best results reported. The ^{19}F nmr spectra were recorded at ambient temperature on 80 mole % $CFCl_3$ solutions utilizing a Varian XL-100-15 spectrometer operating at 94.1 MHz. The ^1H nmr spectrum was obtained at ambient temperature on a Varian EM-360 spectrometer operating at 60 MHz with TMS as an external standard. Ir spectra were obtained on either a Perkin-Elmer model 180 or 337 spectrometer using a 10cm gas cell fitted with AgCl windows. One spectrum, $(C_6F_5O)_2CO$, was recorded in CCl_4 between AgCl plates. Mass spectra were obtained on a AEIMS9 mass spectrometer operating at 70eV with a source temperature of 200°.

Reagents

Potassium pentafluorophenoxide was prepared by a modification of the literature method [4] and dried thoroughly under high vacuum with gentle heating. The acid fluorides $CF_3C(O)F$ and $CH_3C(O)F$ were obtained from P.C.R. Inc. and used without further purification. Carbonyl Fluoride and $CF_3OOC(O)F$ were synthesized by literature methods.[5]

REACTIONS: TABLE I

Most reactions were carried out in a 100 ml glass bulb equipped with a Teflon/glass valve. The usual procedure was to condense the appropriate amount of the acid fluoride onto a known amount of KOC_6F_5 at -195°. The reaction mixture was allowed to warm to 23° and stand for the time indicated (TABLE I). The reaction bulb was cooled to -196 and opened to a pressure gauge. No non-condensables were observed in any of the reactions. The volatile products were distilled into a trap held at -196°. Considerable pumping time is required to remove the lesser volatile materials from the solids remaining in the reaction bulb. Products were separated by trap to trap distillation. In the case of $(C_6F_5O)_2CO$ the reaction was carried out in a sublimation apparatus with a volume of 80 ml. After the removal of volatile products, pure $(C_6F_5O)_2CO$ was easily obtained by sublimation at 95° under high vacuum onto a water cooled cold finger. Caution: after standing at room temperature for about 2 minutes an attempted larger scale preparation of $CF_3OOC(O)OC_6F_5$ (1.5 mmol KOC_6F_5 and 4.16 mmol $CF_3OOC(O)F$) resulted in

TABLE 1

Reactions of KOC_6F_5 with acid fluorides

KOC_6F_5 [e]	Reactant [e]	Conditions	Products [e]	Yield [d]
0.75	1.25 $CF_3C(O)F$	10 min, 23°	0.71 $CF_3C(O)OC_6F_5$ 0.45 $CF_3C(O)F$	96%
1.07	2.18 $CH_3C(O)F$	10 min, 23°	1.00 $CH_3C(O)OC_6F_5$ [a] 1.3 $CH_3C(O)F$	93%
1.54	12.41 COF_2	8 min, 23°	0.44 $FC(O)OC_6F_5$ [a] 11.20 COF_2	29%
0.88	2.04 $CF_3OOC(O)F$	3 min, 23°	0.33 $CF_3OOC(O)OC_6F_5$ [b] 1.51 $CF_3OOC(O)F$ + unidentified impurities 0.18 unidentified material	38%
2.71	1.36 COF_2	15 min, 23°	0.57 $(C_6F_5O)_2CO$ [c] 0.60 COF_2	42%

a. Collected at -78

b. Collected at -40

c. Sublimed under vacuum at 95° to a water cooled cold finger.

d. Yield based on KOC_6F_5.

e. Amounts in mmols.

a confined explosion accompanied by a bright orange flash and complete charring of products. Some physical and spectral data for the prepared compounds is summarized below.

$CF_3C(O)OC_6F_5$: clear liquid at 23°; mp 3.1 to 3.6°; bp 133°; log P (mm) = 7.6848 - 1704.5/T - 10076/T^2; ΔHvap 10.07 kcal/mole; ΔSvap 24.8 eu; mol wt 275.9, calcd. 280.1; ir 3090 (vw) 3050 (vw), 1832 (s), 1525 (s), 1472 (w), 1338 (w), 1320 (w), 1245 (s), 1199 (s), 1155 (vw), 1128 (w), 1102 (s), 1034 (m), 1029 (s), 1012 (m), 993 (m), 871 (w), 760 (w), 683 (w), 672 (m), 662 (w), 658 (m), 640 (w); mass spectrum, molecular ion at m/e = 280.

$CH_3C(O)OC_6F_5$: white solid at 23°; mp 29.8 to 30.2°; vp data, 2.8 mm (solid) (20.1°), 10.8 mm (57.21°), 24.3 mm (74.4°), 37.6 mm (83.8°), 48.9 mm (89.08°); ir 1813 (m), 1524 (s), 1371 (w), 1235 (m), 1180 (s), 1148 (vw), 1025 (m), 1008 (m), 991 (m), 943 (vw), and 858 (w); mass spectrum, molecular ion at m/e = 226.

$FC(O)OC_6F_5$: clear liquid at 23°; mp -6.4° to -6.8; bp 125.8°; log P (mm) = 9.2645 - 2881.6/T + 13361/T^2; ΔHvap 10.12 kcal/mole; ΔSvap 25.4 eu; mol wt 231.1, calcd. 230.1; ir 1874 (m), 1832 (vw), 1652 (vw), 1530 (s), 1478 (vw), 1275 (vw), 1239 (s), 1201 (w), 1158 (vw), 1100 (w), 1037 (m), 1012 (m), 995 (w), 948 (m), 765 (w); mass spectrum, molecular ion at m/e = 230.

$(C_6F_5O)_2CO$: white solid at 23°; mp 49.3 to 49.8°; vp < 1 mm (23°); sublimes easily under vacuum at 95°; ir 1865 (m), 1860 (m), 1530 (s), 1526 (s), 1212 (s), 1120 (vw), 1040 (w), 1003 (s), 980 (s), 948 (m), 895 (vw), 440 (vw); mass spectrum, molecular ion at m/e = 394.

$CF_3OOC(O)OC_6F_5$: clear liquid at 23°; forms clear glass at low temperature; bp 144.8°; log P (mm) = 11.637 - 4614.4/T + 398990/T^2; ΔHvap 12.38 kcal/mole; ΔSvap 29.6 eu; mol wt 332.9, calcd. 312.1; ir 1865 (m), 1730 (vw), 1703 (vw), 1652 (vw), 1530 (s), 1481 (vw), 1325 (w), 1295 (m), 1241 (s), 1164 (s), 1103 (vw), 1080 (vw), 1037 (w), 1008 (m), 969 (w), 943 (w), 883 (vw), 760 (vw).

RESULTS AND DISCUSSION

The reaction of KOC_6F_5 with acid fluorides provides a convenient method for the synthesis of pentafluorophenyl esters in variety. The replacement of reactive halogen atom by OC_6F_5 appears to be quite general [6].

A mechanism involving nucleophilic displacement of F^- has been suggested in the formation of $C_4F_9OC(O)X$ derivatives from KOC_4F_9 and acid halides [2]. The same type of process is thought to be applicable to the formation of $C_6F_5OC(O)X$ compounds by the analogous reaction. Generally higher yields are obtained with considerable shorter reaction times and lower pressure of acid halides in the formation of $C_6F_5OC(O)X$ derivatives. This suggests that $^-OC_6F_5$ is a more active nucleophile than is $^-OC_4F_9$. An increase in the amount of acid halide increases the yield of all esters in comparable reaction times with the logical exception of $(C_6F_5O)_2CO$. The mono-substituted compound, $FC(O)OC_6F_5$, was not observed as a product in reactions not employing excess COF_2.

The new pentafluorophenyl esters are all stabile at 23° in glass and with the exception of $CF_3OOC(O)OC_6F_5$ display molecular ions in the mass spectrum. The lack of a molecular ion in the case of $CF_3OOC(O)OC_6F_5$ is in concurrence with the generally observed results for other perfluoroperoxy compounds [7].

The ir spectra are consistent with the assigned structures of the esters. The presence of the pentafluorophenyl group is strongly indicated by the absorption bands at 1530 cm^{-1} and in the 1000 cm^{-1} region [4]. The carbonyl stretching frequency is also obvious in each molecule and shifted to higher energy with increasing electronegativity of the attached groups "X" (TABLE 2).

TABLE 2

Carbonyl Stretching Frequencies of $C_6F_5OC(O)X$

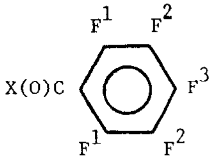
ν C = O	X
1874	F
1865	CF_3OO
1865, 1860	C_6F_5O
1832	CF_3
1813	CH_3

If inductive effects predominate, this behavior may be rationalized. There should be a decrease in the importance of ionic canonical structures with increasing electron withdrawing power of the X group. Therefore, an increase in the double bond character and stretching frequency of the carbonyl bond results [1].

Nmr data for the pentafluorophenyl esters is summarized in TABLE 3. The chemical shift value observed for the "X" portion of the molecule corresponds well with the observed shifts of these groups in similar compounds [8]. The value observed for the CF_3OO fluorines is particularly characteristic [7]. The nmr signals due to the fluorines on the pentafluorophenyl group have the usual relative magnitude of chemical shifts normally found in C_6F_5X systems with $\phi_o < \phi_p < \phi_m$ where o, p, and m are with respect to the X group [9]. This order was established by relative areas of the observed peaks as well as the magnitude and multiplicity of the observed coupling constants. The spectra are broad and the only coupling constants resolved involve fluorines which are ortho to each other on the ring. This is not unexpected as the magnitude of fluorine-fluorine coupling constants in aromatic systems are generally of the order ortho > para > meta [9].

TABLE 3

^{19}F Nmr Data



$X^{a,b}$	ϕ_X	ϕ_{F^1}	ϕ_{F^3}	ϕ_{F^2}	$J_{F^1F^2}$	$J_{F^2F^3}$
F	22.6	154.1	156.1	161.8	15.6	20.6
CF_3OO	69.5	153.9	156.1	161.9	15.6	20.7
C_6F_5O	--	153.9	156.7	162.2	16.5	20.7
CF_3	74.7	153.4	156.0	161.9	16.0	21.0
CH_3	$2.05(^1H)^c$	154.0	159.6	164.1	19.0	22.0

a. chemical shifts in ppm relative to internal $CFCl_3$

b. coupling constants in Hz

c. relative to external TMS

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