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(10) *Anal.* Calcd (found): C, 42.26 (41.13); H, 3.33 (3.33). Mass spectrum: parent ion at *m/e* 851 ± 1 (852 calcd). Ir (Nujol mull, cm^{-1}): 1137 (w), 1074 (w), 1040 (m), 1027 (ms), 872 (w), 852 (w), 787 (vs, br). The poor solubility has precluded the observation of a pmr spectrum, even with CW time averaging.
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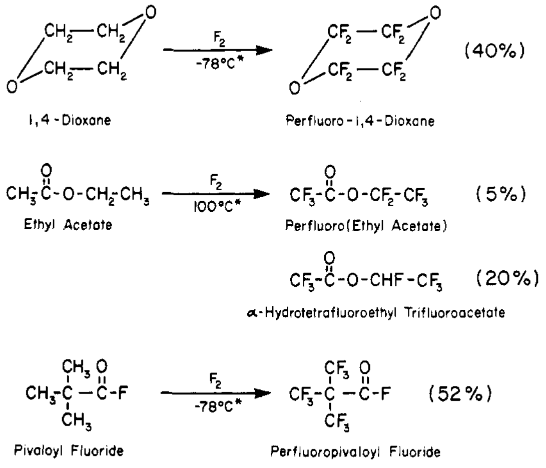
Synthesis of Perfluoro-1,4-dioxane, Perfluoro(ethyl acetate), and Perfluoropivaloyl Fluoride by Direct Fluorination

Sir:

Recent advances in direct fluorination[1-3] will make possible the synthesis of many important new oxygen-containing functional fluorocarbon molecules and provide a valuable synthetic route to complement existing synthetic methods. To demonstrate this potential for handling three separate functional groups, we wish to report the first successful fluorination of 1,4-dioxane, of pivaloyl fluoride, $(CH_3)_3CCFO$, and of a hydrocarbon ester to produce the corresponding perfluorocarbon analogs (see Chart I) in good yields.

Chart I. Reactions



*Lowest temperature of gradient

Previous attempts to fluorinate 1,4-dioxane electrolytically in anhydrous hydrogen fluoride yielded the acyclic ether perfluoro-1,2-dimethoxyethane in 4% yield but no perfluoro-1,4-dioxane.[4] Perfluoro-1,4-dioxane has been prepared previously in 4% yield by dimerization of tetrafluoroethylene oxide.[5]

Only recently have studies indicated that acyclic perfluoroesters and α-hydrofluoroesters are stable as a class of compounds.[6-8] However, no direct synthesis of a perfluoroester from a hydrocarbon ester has been reported previously. Perfluoropivaloyl fluoride has not been prepared.

The direct fluorination of acyl fluorides as a class of compounds represents an important route to the perfluoroacids. Pivaloyl fluoride was selected as an example of a sterically crowded system which is difficult to prepare by other methods.[9]

In a typical experiment for the preparation of perfluoro-1,4-dioxane a 3.3-g sample of 1,4-dioxane was evaporated over a 20-hr period by a 160-cm^3/min flow of helium into a four-zone cryogenic reactor[2] which was maintained at 0°. The reactor was cooled to −78° and a 0.5 cm^3/min flow (approximately 30 mmol per day) of fluorine diluted with a 20-cm^3/min flow of helium was passed over the solid dioxane. After 12 hr, the rate was increased to 1.0 cm^3/min for 1 day and then further increased to 1.5 cm^3/min where it was maintained for 6 days. During this period the helium flow was reduced to zero, and reactor zones one through four were warmed sequentially to their equilibrium temperature until all were at ambient at the end of the 6-day period. Similar programs were used for ethyl acetate and pivaloyl fluoride. The crude product was hydrolyzed in 2.0 *M* KOH, separated from the aqueous layer and fractionated. Glc assay of the contents of the −95 and −131° traps yielded 3.37 g (38.5%) of perfluoro-1,4-dioxane and 0.4 g (4%) of perfluoro-1,2-dimethoxyethane. The −196° trap contained 4.23 g (58%) of essentially pure perfluorodimethyl ether.

Anal. Calcd for $C_4F_8O_2$: C, 20.706; F, 65.503. Found: C, 20.63; F, 65.67.

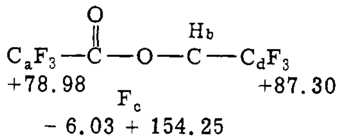
Perfluoro-1,4-dioxane is a gas at room temperature (bp 15.9°). The molecular weight determined by the ideal gas method was 232.7, *vs.* 232.0 for $C_4F_8O_2$. The ^{19}F nmr consisted of a singlet at φ +90.78 ppm (relative to $CFCl_3$, external). The infrared spectrum exhibits bands at 1435 (w), 1369 (w), 1311 (sh), 1303 (s), 1232 (vs), 1163 (sh), 1149 (s), 1113 (3), 890 (m), 665 (m) wave numbers. The mass spectrum shows no parent peak but shows a peak at *m/e* 213 corresponding to the molecular ion minus a fluorine $C_4F_7O_2$. Other strong peaks are *m/e* 119 (C_2F_5), *m/e* 100 (C_2F_4), *m/e* 69 CF_3, *m/e* 50 (CF_2), and *m/e* 47 (CFO).

In the preparation of perfluoro(ethyl acetate) a 1.74-g sample of ethyl acetate was admitted into a four-zone gradient reactor[2] with zones cooled to −100°. After the fluorination procedure, the product was collected, fractionated, and purified by glc (fluorosilicone QFl-0065 13% on Chromasorb p) yielding the following products: $CF_3CO_2C_2F_5$, 0.23 g (5%); $CF_3CO_2CHFCF_3$, 0.85 g (20%); $CF_3CO_2CF_2CF_2H$, 0.05 g (1.2%); FCO_2CHFCF_3, 0.5 g (1.4%); also the −196° trap contained 2 g of a mixture of about equal parts CF_3CFO and CHF_2CFO.

Anal. Calcd. for $C_4F_8O_2$: C, 20.706; F, 65.503. Found: C, 20.65; F, 65.48.

Perfluoro(ethyl acetate) is a moisture sensitive gas (bp 21.4°) which easily rearranged to 2 mol of trifluoroacetyl fluoride. The infrared spectrum and ^{19}F nmr are in agreement with that published by Shreeve and coworkers.[6] The major product isolated from the reaction of ethyl acetate and elemental fluorine is the trifluoroacetic acid ester of the unstable alcohol α-hydrotetrafluoroethyl alcohol. This fluoro alcohol ester is a moisture sensitive liquid (bp 31.7°) which can be converted by a Lewis base into a equimolar mixture of trifluoroacetyl fluoride and trifluoroacetaldehyde. The product was identified by a molecular weight determination (214.2, *vs.* 214 for $C_4F_7HO_2$), infrared, and ^{19}F and ^1H nuclear magnetic resonance. The infrared spectrum exhibits bands at 2995 (w), 1830 (s), ($\nu C{=}O$), 1420 (w), 1370 (w), 1331 (w), 1300 (s), 1248 (s), 1218 (vs), 1198 (vs), 1140 (s), 1105 (vs), 1062 (m), 920 (m), 733 (m), 698 (m), 628 (w), 580 (w), 550 (w) cm^{-1}. The ^{19}F and ^1H nuclear magnetic resonance spectrum is summarized in Chart II. A major factor affecting yields in this reaction is presumed to be the rearrangement of perfluoro(ethyl acetate) to two moles of trifluoroacetyl fluoride catalyzed by hydrogen fluoride which is produced in the reaction. If this problem were overcome the quantity of ester recovered could increase markedly. The β-hydrotetrafluoroethyl trifluoroacetate was also fully characterized.

Chart II



$$\underset{+78.98}{C_aF_3}-\overset{\overset{\displaystyle O}{\|}}{C}-O-\underset{\underset{-6.03\ +154.25}{F_c}}{\overset{H_b}{C}}-\underset{+87.30}{C_dF_3}$$

$J_{ab} = {\sim}0\ Hz$

$J_{ac} = 0.5\ Hz$

$J_{bc} = 50.53\ Hz$

$J_{bd} = 3.05\ Hz$

$J_{cd} = 5.87\ Hz$

The yields of the most important by-products CF_3CFO and CHF_2CFO are often obtained in yields as high as 40%; CF_4, OCF_2, and possibly $FCO_2C_2F_5$ are also produced in the reaction.

For the preparation of *perfluoropivaloyl fluoride,* a 2-ml sample (1.961 g, 0.0188 mol) was injected into the evaporator of the fluorination reactor (a six-zone modification).[2] The reactor was cooled to −78° during the fluorination procedure.

A crude yield of 4.4 g of material containing perfluoroisobutane, perfluoro-3,3-dimethyl-1-oxacyclobutane, perfluoropivaloyl fluoride, and monohydrooctafluoropivaloyl fluoride was obtained. From this mixture, 2.6 g (52% yield) of perfluoropivaloyl fluoride was isolated. The monohydroacyl fluoride still makes up approximately 20% of the molar yield, the other two products making up most of the remaining material. Perfluoropivaloyl fluoride is a very volatile solid (mp 38–38.5° sealed tube) which sublimes readily at room temperature. The product has been characterized by ^{19}F nmr (a 95% solution in CCl_4) and consists of a dectet (J = 11.5 Hz) centered at −42.34 ppm and a doublet (J = 11.4 Hz) centered at +67.08 ppm relative to external $CFCl_3$–CCl_4. The relative integrals were 1:9.5. The mass spectrum exhibits a molecular ion at *m/e* 266, a P − F at *m/e* 247, a P − COF_2 at *m/e* 200, and other strong peaks at *m/e* 181 ($C_4F_7^+$), 178 ($C_4F_6O^+$), 159 ($C_4F_5O^+$), 131 ($C_3F_5^+$), 69 (CF_3^+) (strongest peak), and 47 (COF_2^+).

The infrared spectrum exhibits bands at 1880 (m) (ν(C–O)), 1855 (sh), 1312 (sh), 1290 (vs), 1215 (m), 990 (s), 739 (w), 710 (w), 660 (w), and 540 (w) wave numbers.

Anal. Calcd for $C_5F_{10}O$: C, 22.574; F, 71.412. Found: C, 22.38; F, 71.26.

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The Size of Phosphorus Ligands. An Experimental Proton Magnetic Resonance Technique for Determining Cone Angles

Sir:

There is a clear nonlinear relationship between the shift of the methyl resonance of coordinated methanol (σ_{MMR}) and the "bulkiness" or "steric size" of the L ligand in *trans*-$[LCo(DH)_2(CH_3OH)]^+$, where L = RR'_2P (R = or ≠ R′ = alkyl, aryl, alkoxy, or phenoxy) and DH = monoanion of dimethylglyoxime, $HONC(CH_3)C(CH_3)NO^-$ (Table I). Steric effects of trivalent phosphorus ligands can dominate the chemistry of NiL_4 complexes.[1,2] A steric parameter, the cone angle (CA, hereafter referred to as TCA), was defined by Tolman.[1] These angles have been correlated with a wide variety of phenomena including stabilities,[3] fluxional behavior,[4] rate constants,[5] catalytic activities,[6] and specificities[6] in product formation. Electronic effects of L are also inherent in such phenomena. From the data in Table I it is clear that a good correlation exists between σ_{MMR} in $LCo(DH)_2(CH_3OH)^+$ and the TCA of L. At low TCA, <120°,