354, 326, 298, 281, 227, 199, 171, 155, 139. On the Hewlett-Packard instrument, two peaks of equal area appeared; molar responses equal to that of **3** were assumed.

Kinetics Experiments. A weighed amount of KBr was added to the ammonia containing the nucleophile (formed in the usual manner). The flask was covered with tape and foil, and all lights in the laboratory were extinguished. The dihalobenzene was then added. Samples were removed by means of a small glass ladle at measured times and quenched by addition to a beaker containing water, ether, and a crystal of ammonium nitrate. The water layer was titrated potentiometrically with silver nitrate, and the amounts of iodide and bromide ions were estimated from the respective end points. Since the bromide ion concentration was known, this procedure amounted to a determination of the iodide ion concentration. The slopes of the lines in the plotted graphs of $\ln[(b-2x)/(a-x)]$, $\ln[(b-x)/(a-x)]$, $\ln(a_\infty - a_t)$, or $\ln(b_\infty - b_t)$ vs. time where $a = [XC_6H_4I]_0$ and $b = [(EtO)_2PO^-Na^+]_0$ were determined by linear-regression analysis. The rate constants were calculated from the slopes. Only rate constants derived from plots of $\ln[(b-x)/(a-x)]$ vs. time are listed in Table III.

Acknowledgment. This research was supported in part by the National Science Foundation. Acquisition of the Finnigan Model 4000 GC/MS equipment was assisted by the NSF Chemical Instrumentation Program.

Registry No. 1b, 583-55-1; **1c**, 615-41-8; **1f**, 348-52-7; **1i**, 615-42-9; **2c**, 28036-18-2; **2f**, 312-05-0; **2h**, 1754-49-0; **2i**, 71838-14-7; **3**, 71838-15-8; **4**, 71838-16-9; **5**, 71838-17-0; 3-bromo-4-aminotoluene, 583-68-6; diethyl phosphite anion, 29800-93-9; I^-, 20461-54-5; Br^-, 24959-67-9; *m*-bromotoluene, 591-17-3; *m*-toluidine, 108-44-1; *p*-toluidine, 106-49-0; diethyl *p*-tolylphosphonate, 1754-46-7; diethyl *m*-tolylphosphonate, 15286-13-2; diethyl 2-iodo-4-methylphenylphosphonate, 71838-18-1; diethyl 2-iodo-5-methylphenylphosphonate, 71838-19-2; PhF, 462-06-6; PhCl, 108-90-7; PhBr, 108-86-1; PhI, 591-50-4; $H_2NPO(OEt)_2$, 1068-21-9; $PhNH_2$, 62-53-3; Cl^-, 16887-00-6.

Some New Reactions of Perfluorinated Sulfonic Acids

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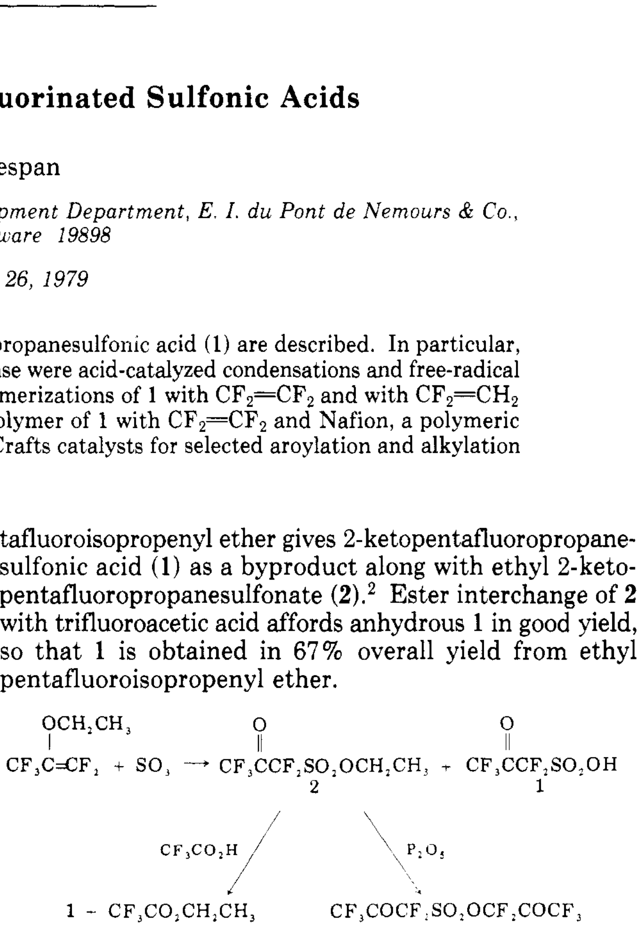
The synthesis and some chemistry of 2-ketopentafluoropropanesulfonic acid (1) are described. In particular, reactions at the carbonyl group of 1 found to proceed with ease were acid-catalyzed condensations and free-radical additions. The latter reaction was adapted to vinyl copolymerizations of 1 with $CF_2{=}CF_2$ and with $CF_2{=}CH_2$ to prepare new sulfonated fluoro polymers. Both the copolymer of 1 with $CF_2{=}CF_2$ and Nafion, a polymeric perfluorosulfonic acid, are shown to be promising Friedel–Crafts catalysts for selected aroylation and alkylation reactions.

Perfluoroalkylsulfonic acids are exceptionally strong acids and function as Friedel–Crafts catalysts. A striking example of the latter is the demonstration by Effenburger and Epple[1] that aroylation of aromatic nuclei with aroyl chlorides is effectively catalyzed by trifluoromethanesulfonic acid. Our recent synthesis of 2-ketopentafluoropropanesulfonic acid (1)[2] prompted a study of the chemistry of 1 with the aim of incorporating this readily available sulfonic acid into fluoro polymers by reaction at its carbonyl group. The sulfonated fluoro polymers so obtained might be valuable catalysts for reactions known to be promoted by trifluoromethanesulfonic acid or by conventional catalysts such as aluminum chloride. Among the advantages possible with insoluble polymeric catalysts are the use of truly catalytic rather than molar amounts of catalyst, ease of product workup, and reuse of catalyst on a continuous or batchwise basis. Results in the test cases detailed below indicate that such advantages can be realized with sulfonated fluoro polymers of sufficiently low equivalent weight.[3]

Results and Discussion

Synthesis of 2-Ketopentafluoropropanesulfonic Acid (1). The reaction of sulfur trioxide with ethyl pentafluoroisopropenyl ether gives 2-ketopentafluoropropanesulfonic acid (**1**) as a byproduct along with ethyl 2-ketopentafluoropropanesulfonate (**2**).[2] Ester interchange of **2** with trifluoroacetic acid affords anhydrous 1 in good yield, so that 1 is obtained in 67% overall yield from ethyl pentafluoroisopropenyl ether.



An attempt to convert ester **2** directly to the sulfonic anhydride by heating in the presence of phosphoric anhydride resulted in loss of sulfur dioxide as well as ethylene. No sulfonic anhydride was detected, and the volatile product obtained was the perfluorinated sulfonic ester **3**.[4]

Derivatization of 1. As a very strong acid, 1 is capable of adding to vinylidene fluoride, even at temperatures well below 0 °C. Protonation occurs readily to give a polar intermediate with well-stabilized charges; subsequent

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(1) F. Effenberger and G. Epple, *Angew. Chem., Int. Ed. Engl.*, 11, 300 (1972).

(2) C. G. Krespan, B. E. Smart, and E. G. Howard, *J. Am. Chem. Soc.*, 99, 1214 (1977).

(3) A recent paper by Olah et al. (G. A. Olah, R. Malhotra, S. C. Narang, and J. A. Olah, *Synthesis*, 672 (1978)) reports similar conclusions.

(4) F. Effenberger and K. Huthmacher, *Angew. Chem., Int. Ed. Engl.*, 13, 409 (1974), describe thermolyses of fluorinated sulfonic anhydrides which appear to proceed by heterolytic fission, loss of SO_2, and recombination to give esters.

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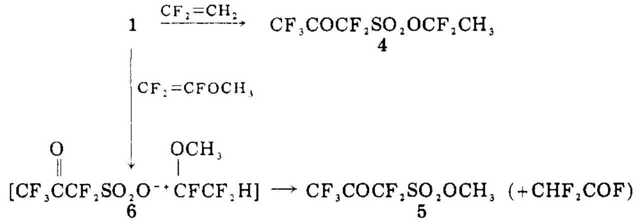
combination leads to the 1,1-difluoroethyl ester 4 in high yield. Unlike the addition of fluorosulfonic acid to vinylidene fluoride reported by Olah and Mo,[5] the addition of 1 was carried out without superacid medium.



$$
\begin{array}{l}
1 \xrightarrow{\mathrm{CF_2=CH_2}} \underset{\mathbf{4}}{\mathrm{CF_3COCF_2SO_2OCF_2CH_3}} \\
\quad\Big\downarrow \mathrm{CF_2=CFOCH_3} \\
\underset{\mathbf{6}}{[\mathrm{CF_3}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{CF_2SO_2O^{-}\,{}^{+}}\overset{\mathrm{OCH_3}}{\overset{|}{\mathrm{C}}}\mathrm{FCF_2H}]} \longrightarrow \underset{\mathbf{5}}{\mathrm{CF_3COCF_2SO_2OCH_3}}\ (+\mathrm{CHF_2COF})
\end{array}
$$

Another and probably more general route to esters of 1 is exemplified by the synthesis of methyl 2-ketopentafluoropropanesulfonate (5). Methyl trifluorovinyl ether reacts exothermically with acid 1 to give 5 in 83% yield, presumably via polar intermediate 6, an ion pair in which the cation is a potent methylating agent capable of transferring methyl to the fluoroalkylsulfonate anion. Ion pair 6 is comparable to the dipolar intermediate 7 which

$$
\underset{\mathbf{7}}{\mathrm{CF_3}\underset{+}{\overset{\mathrm{OC_2H_5}}{\overset{|}{\mathrm{C}}}}\mathrm{CF_2SO_2O^-}} \qquad \underset{\mathbf{8}}{\mathrm{FSO_2O^-\,{}^{+}}\overset{\mathrm{OCH_3}}{\overset{|}{\mathrm{C}}}\mathrm{FCHFCF_3}}
$$

we have demonstrated to be the precursor of ethyl ester 2.[2] Our reaction of sulfur trioxide with an alkyl polyfluoroalkyl ether to form fluorinated acid fluoride and alkyl fluorosulfate[6] is also explicable on the basis of an ion pair (e.g., 8) generated by attack of sulfur trioxide on fluorine α to the ether oxygen. The alternative of attack at oxygen and migration of methyl cation would be expected to give a sulfonate ester as a stable product. Fluorovinyl ethers may become the reagents of choice for the esterification of very strong acids, since the reaction can be difficult or dangerous with the usual reagents but proceeds easily and to completion with methyl trifluorovinyl ether.

Conversion of 1 to the sulfonyl chloride 9 was accomplished with phosphorus pentachloride but in low yield. This reaction may require coreagents such as zinc chloride, as recommended by Tiers,[7] and stoichiometric amounts of reactants for reasonable yields. The elemental analysis suggests that replacement of the carbonyl oxygen in 9 with chlorine is an unwanted side reaction.

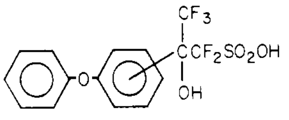
$$1 \xrightarrow{\mathrm{PCl_5}} \underset{\mathbf{9}}{\mathrm{CF_3COCF_2SO_2Cl}}$$

Reactions directed toward the carbonyl group in 1 can be catalyzed by strong acid as condensations with hexafluoroacetone are. Early work[8] on Friedel–Crafts condensations using hexafluoroacetone extends to the benzene case with trifluoromethanesulfonic acid as catalyst. The only product isolated, even at high temperature, is 80% of the 1:1 adduct α,α-bis(trifluoromethyl)benzyl alcohol (10).

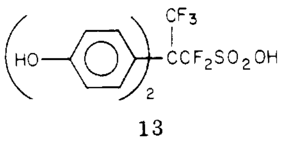
$$\mathrm{C_6H_6} + \mathrm{CF_3COCF_3} \xrightarrow[160\ ^\circ\mathrm{C}]{\mathrm{CF_3SO_2OH}} \underset{\mathbf{10}}{\mathrm{C_6H_5C(CF_3)_2OH}}$$

Anhydrous 1, with the catalytic function built into the molecule, undergoes a mildly exothermic reaction with benzene to form adduct 11, isolated as its pyridinium salt. Similarly, addition of 1 to diphenyl ether under mild conditions gave 12 (probably the para isomer). Condensation of 1 with phenol at elevated temperature resulted in bis substitution with 13 as the major product. Molecules such as 12 and 13 offer possibilities for further condensations to sulfonated polymers, but these have not been investigated.

$$\mathrm{C_6H_6} + 1 \longrightarrow \underset{\mathbf{11}}{\mathrm{C_6H_5C(CF_3)(OH)CF_2SO_2OH}}$$



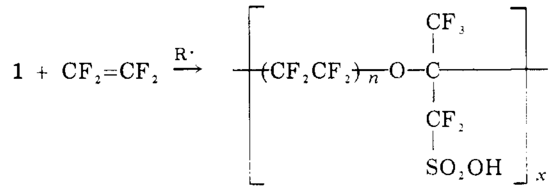
12



13

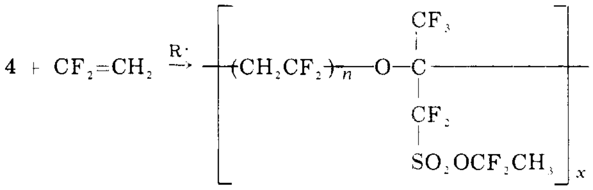
Autocatalyzed reaction of 1 with polystyrene also occurred. Introduction of strongly acidic sulfonic acid groups, presumably onto phenyl groups near the surface of the polymer particles, occurred when cross-linked polystyrene was stirred at 25 °C with a 1,1,2-trichlorotrifluoroethane solution of 1.

Copolymerization of 1. Hexafluoroacetone and related fluoro ketones add free radicals at the carbonyl group,[9] and this reaction allows incorporation of fluoro ketone directly into polymers by radical-catalyzed copolymerization with vinyl monomers. 1 copolymerizes with the vinyl monomers tetrafluoroethylene and vinylidene fluoride. Tetrafluoroethylene and anhydrous 1 react in an inert medium at moderate to high pressures with free-radical initiation to form high polymers containing limited amounts of 1. Incorporation of 1 evidently occurs normally by reaction at the carbonyl group, since very stable dyings were obtained with a cationic dye. The levels of color correlated with the sulfur analyses, which indicated up to 2 wt % of 1 was incorporated.



$$1 + \mathrm{CF_2=CF_2} \xrightarrow{\mathrm{R}\cdot} \left[-\!\!\left(\mathrm{CF_2CF_2}\right)_{n}\!-\mathrm{O}-\underset{\underset{\mathrm{SO_2OH}}{|}}{\underset{\mathrm{CF_2}}{\underset{|}{\overset{\overset{\mathrm{CF_3}}{|}}{\mathrm{C}}}}}- \right]_x$$

Early copolymerizations of 1 with vinylidene fluoride were complicated by the preliminary formation of sulfonate ester 4. Better control of the reaction was achieved by copolymerization of preformed 4 with vinylidene fluoride. Reaction of the propagating radical-chain end with the carbonyl group occurs readily in this case, so that levels of 1 up to 40 wt % were easily incorporated. Polymers ranging from solids of low solubility to amorphous materials soluble in 1,1,2-trichlorotrifluoroethane were formed, depending upon the ratio of comonomers in the reaction.



$$4 + \mathrm{CF_2=CH_2} \xrightarrow{\mathrm{R}\cdot} \left[-\!\!\left(\mathrm{CH_2CF_2}\right)_{n}\!-\mathrm{O}-\underset{\underset{\mathrm{SO_2OCF_2CH_3}}{|}}{\underset{\mathrm{CF_2}}{\underset{|}{\overset{\overset{\mathrm{CF_3}}{|}}{\mathrm{C}}}}}- \right]_x$$

Friedel–Crafts Catalysis. The system p-xylene/benzoyl chloride was selected to test the activity of copolymer $1/\mathrm{CF_2{=}CF_2}$ as a Friedel–Crafts catalyst. Despite its very high (>10 000) equivalent weight, the copolymer slowly produced 2,5-dimethylbenzophenone in a clean reaction at 140 °C.

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(5) G. A. Olah and Y. K. Mo, *J. Org. Chem.*, 37, 1028 (1972).

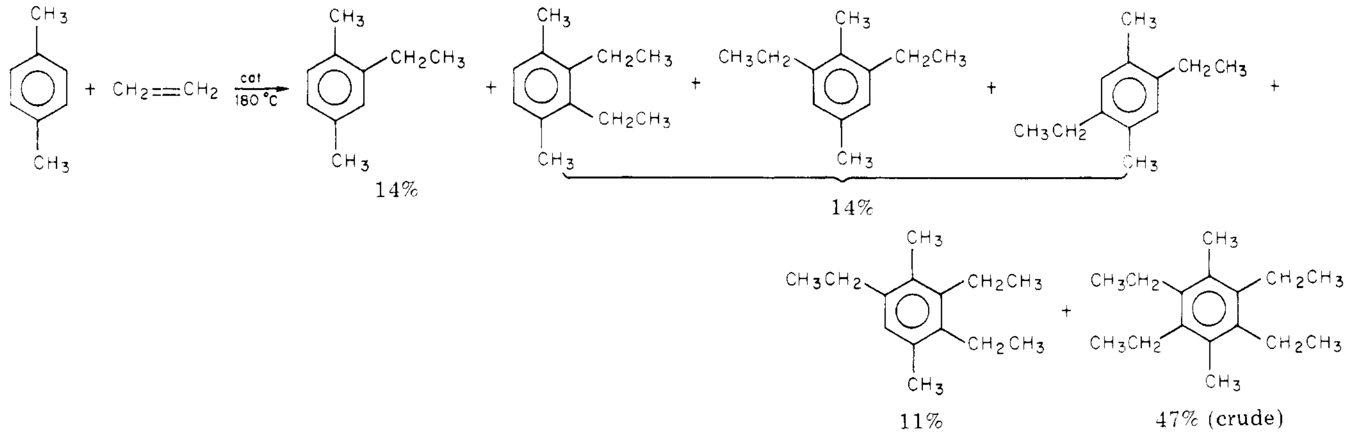
(6) D. C. England, L. Solomon, and C. G. Krespan, *J. Fluorine Chem.*, 3, 63 (1973/74).

(7) G. V. D. Tiers, *J. Org. Chem.*, 28, 1244 (1963).

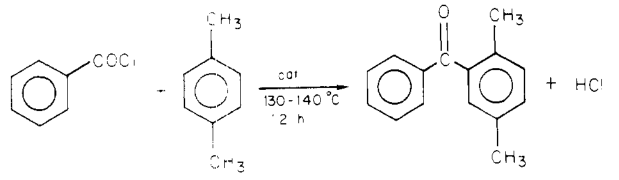
(8) Dr. W. Schindel (Organic Chemicals Dept., E. I. du Pont de Nemours) first demonstrated that alkylation of aromatic compounds with hexafluoroacetone is efficiently catalyzed both by 1,1,2,2-tetrafluoroethanesulfonic acid and by Nafion sulfonated fluoro polymer.

(9) E. G. Howard, P. B. Sargeant, and C. G. Krespan, *J. Am. Chem. Soc.*, 89, 1422 (1967).

Scheme I



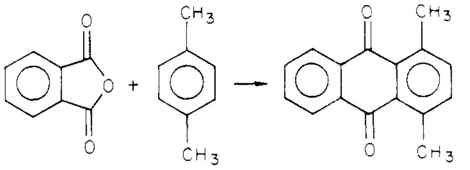
For further demonstrations that polymeric fluoroalkylsulfonic acids can be of value as Friedel–Crafts catalysts, Nafion[10] was chosen as the test catalyst because of its availability and low equivalent weight as well as its known chemical and thermal stability. As a catalyst for aroylation with aroyl chlorides, Nafion perfluorosulfonic acid polymer (Nafion H) performed well as a true catalyst. Benzoylation of *p*-xylene at 135 °C was accomplished in 85% yield in the presence of only small amounts of Nafion H beads of equivalent weight 1100. The product, 2,5-dimethylbenzophenone, was isolated by simple filtration and distillation. The catalyst, separated by filtration, was recycled without noticeable loss in activity, suggesting only slow deactivation through side reactions. The insoluble catalyst showed markedly lower activity at temperatures below about 100 °C, as judged by very slow evolution of HCl. An increase in the equivalent weight of Nafion H catalyst to only 1790 resulted in a marked decrease in rate of reaction.



Similar reactant combinations of *p*-xylene/*p*-nitrobenzoyl chloride at 140 °C, 1,4-dimethoxybenzene/benzoyl chloride at 100–120 °C, and ethylbenzene/*p*-chlorobenzoyl chloride at 105 °C produced diaryl ketones in moderate yields from single experiments. High yields could almost certainly be obtained with further study.

In view of the results previously obtained with trifluoromethanesulfonic acid and aroyl halides,[1] the formation of mixed anhydrides as intermediates in the present case is a reasonable assumption. The lowered reactivity encountered in using a very negatively substituted acid chloride such as pentafluoropropionyl chloride is therefore not surprising. Reaction with toluene proceeded slowly even at 180 °C.

Complications occurred with phthaloyl derivatives. Condensation of phthaloyl chloride with *p*-xylene at 140–145 °C gave off limited amounts of HCl and formed black reaction mixtures. On the other hand, reaction of phthalic anhydride with *p*-xylene led mainly to recovered starting materials, with a low yield of 1,4-dimethylanthraquinone formed. Although the sulfonated catalyst may be inactivated toward further reaction with phthalic anhydride by coordination to the product formed, it retained its ability to catalyze the condensation of benzoyl chloride with *p*-xylene.



An indication that anhydrides as a class react normally is provided by the addition of propionic anhydride to α-naphthol. The product, whether obtained by Fries rearrangement[11] or direct acylation, was 73% 1-hydroxy-2-propionaphthone. The ability of the catalyst to tolerate acidic products in this case is similar to that noted in the formation of fluoro alcohols from hexafluoroacetone and aromatics.

Alkylation of aromatic compounds is also catalyzed by Nafion sulfonated fluoro polymer.[12] Reaction of ethylene with *p*-xylene at 100 °C and 1500 psi appears negligible, but proceeded slowly at 150 °C and 2500 psi to give 7% conversion of *p*-xylene to 1,4-dimethyl-2-ethylbenzene, isolated after 14 h. Only minor amounts of higher alkylated products were formed at 150 °C, but at 180 °C and 1700 psi reaction proceeded steadily over 8 h to give the products shown in Scheme I.

The results indicate that good yields of the monoalkylated derivative are available at modest conversions of the aromatic compound but that Nafion perfluorosulfonic acid polymer shows a strong tendency to catalyze polyalkylation at high conversions. Such low selectivity is common with Friedel–Crafts catalysts and indeed was also observed with Nafion in the flow system studied by Olah et al.[12] Alkylation in the liquid phase under pressure and with prolonged contact times is clearly most suitable for polyalkylation.

Conclusions

2-Ketopentafluoropropanesulfonic acid can be used as a comonomer in free-radical polymerizations and to introduce fluorinated sulfonic acid groups via condensation

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[10] Nafion is a registered trademark for the sulfonated perfluoro polymer produced by E. I. du Pont de Nemours and Co.

[11] Onada and Wada (T. Onada and K. Wada, Japanese Kokai 7608231 (Jan 23, 1976); *Chem. Abstr.*, 84, 164449 (1976)) report the ability of Nafion H to catalyze the Fries rearrangement.

[12] G. A. Olah, J. Kaspi, and J. Bukala, *J. Org. Chem.*, 42, 4187 (1977), reported on the alkylation of benzene in the vapor phase over a number of solid catalysts. Perfluorinated sulfonic acid resin Nafion H has good catalytic activity and superior stability in reactions of, for example, ethene with benzene. The gas-phase flow systems described in the paper complement the liquid-phase reactions under pressure which were carried out in the present work.

reactions. This functionalized comonomer thus provides easy access to some new polyfluorinated polymers containing sulfonic acid residues. Such polymeric perfluorosulfonic acids, as exemplified by the very stable Nafion H perfluorosulfonic acid polymer, are convenient, effective, and reusable Friedel–Crafts catalysts for both aroylation and alkylation.

Experimental Section

Melting points and boiling points are uncorrected. IR spectra were recorded on a Perkin-Elmer 21 spectrophotometer for a 20% solution in CCl_4 unless otherwise noted. ^{1}H NMR spectra were taken on a Varian A60 spectrometer using 20% solutions in CCl_4 and tetramethylsilane as an internal standard. ^{19}F NMR spectra were taken on a Varian XL 100 spectrometer at 94.1 MHz for 20% solutions in CCl_4 with trichlorofluoromethane as an internal standard; downfield directions are taken as positive.

2-Ketopentafluoropropanesulfonic Acid (1). Characterization of 1 has been reported previously.[2] Large amounts were available by the following transesterification. A mixture of 25.6 g (0.10 mol) of ethyl 2-ketopentafluoropropanesulfonate (2) and 17.1 g (0.15 mol) of trifluoroacetic acid was heated to reflux, and ethyl trifluoroacetate was slowly taken off over a 4-h period; bp 60 °C (1 atm)–41 °C (280 mm). The bath temperature was kept below 100 °C to avoid decomposition reactions which set in near 115 °C. Further distillation gave 18.4 g (81%) of 1, bp 73 °C (2.6 mm).

Preparation on a larger scale from ethyl pentafluoroisopropenyl ether in a one-pot reaction is easy. Addition of 157.6 g (1.97 mol) of SO_3 to 346.2 g (1.97 mol) of ethyl pentafluoroisopropenyl ether at −15 °C required 20 min. The colorless mixture was warmed to ca. 30 °C, where an exotherm developed. The temperature was kept below 50 °C by external cooling. Then 285 g (2.5 mol) of trifluoroacetic acid was added, and the mixture was stirred overnight. Distillation afforded 301.9 g (67% from vinyl ether) of sulfonic acid 1, for which the boiling point was mainly 56 °C (1.6 mm).

Pure samples obtained by redistillation, bp 54 °C (1.4 mm), were stored in bottles of Teflon fluorocarbon resin for subsequent use in copolymerization studies. The anhydrous material is soluble in organic compounds such as 1,1,2-trichlorotrifluoroethane.

2-Ketopentafluoropropyl 2-Ketopentafluoropropanesulfonate (3). A mixture of 25.6 g (0.10 mol) of ester **2** and 25 g of P_2O_5 was heated to ca. 125 °C, where gas evolution became noticeable. The reaction mass was heated at 125–145 °C until gas evolution ceased; at the higher temperature fuming of off-gases was noted. Distillation gave 7.7 g of material: bp 40–55 °C (25 mm). Redistillation afforded 5.3 g (28%) of **3**: bp 50–51 °C (50 mm); IR (CaF_2 plates) 5.53 (C═O), 6.88 (SO_2O), 7.5–8.5 (CF, SO_2) μm; ^{19}F NMR −74.6 (m, 2, OCF_2), −75.0 (t, J_{FF} = 8.0 Hz, atop m, 6, CF_3), −104.2 (rough q, J_{FF} = 8.0 Hz, into overlapping t, J_{FF} = 7.5 Hz, 2, CF_2) ppm.

Anal. Calcd for $C_6F_{10}O_5S$: C, 19.26; F, 50.78. Found: C, 19.31; F, 50.64.

2-Ketopentafluoropropanesulfonyl Chloride (9). The tetrahydrate of 1 (50.0 g, 0.17 mol) was added dropwise over a 2-h period to 248 g (1.2 mol) of PCl_5. Distillation gave 40.9 g of liquid, bp 80–100 °C, which was fractionated to yield 5.9 g (14%) of impure **9**: bp 90–92 °C; IR 5.55 (C═O), 7.05 (SO_2Cl), 7.5–8.5 (CF, SO_2) μm; mass spectrum *m/e* 147 ($M^+ - SO_2Cl$), 97 (CF_3CO^+), 69 (CF_3^+), 64 (SO_2^+) (C_3F_5O peak mass measured at 146.9869 (calcd 146.9869)); ^{19}F NMR −74.9 (t, J_{FF} = 8.0 Hz, 3, CF_3), −101.3 (q, J_{FF} = 8.0 Hz, 2, CF_2) ppm (several impurities were also present).

Anal. Calcd for $C_3ClF_5O_3S$: C, 14.61; Cl, 14.38. Found: C, 14.01; Cl, 18.11.

1,1-Difluoroethyl 2-Ketopentafluoropropanesulfonate (4). A metal tube containing 23.8 g (0.10 mol) of anhydrous acid 1 was cooled below −40 °C, and 13 g (0.20 mol) of vinylidene fluoride was added. The mixture was shaken as it warmed to 25 °C and was kept at 25 °C for 4 h. Distillation of the liquid product gave 20.4 g (70%) of ester **4**: bp 62–63 °C (50 mm); IR 5.54 (C═O), 6.96 (SO_2O), 7.5–9 (CF, SO_2) μm; ^{1}H NMR 2.06 (t, J_{HF} = 14.3 Hz, CH_3) ppm; ^{19}F NMR −58.3 (q, J_{HF} = 14.3 Hz of t, J_{FF} = 14.3 Hz of t, J_{FF} = 7.1 Hz, 2 F, OCF_2), −75.0 (t, J_{FF} = 8.0 Hz, 3 F, CF_3), −106.1 (q, J_{FF} = 8.0 Hz of t, J_{FF} = 7.1 Hz, 2 F, CF_2SO_2).

Anal. Calcd for $C_5H_3F_7O_4S$: C, 20.56; H, 1.03; F, 45.52. Found: C, 20.73; H, 1.03; F, 45.72.

A similar reaction on a 0.8-mol scale gave an 86% yield of **4**, bp 60 °C (50 mm).

Methyl 2-Ketopentafluoropropanesulfonate (5). Neat acid 1 (25.6 g, 0.11 mol) was stirred at 25 °C while excess methyl trifluorovinyl ether was distilled in. *Caution: Methyl trifluorovinyl ether can be detonated and should be used with appropriate shielding.* The ensuing vigorous reaction was controlled under 50 °C by external cooling. Distillation afforded 22.0 g (83%) of methyl ester **5**: bp 56–58 °C (28 mm); IR 3.35 and 3.50 (saturated CH), 5.57 (C═O), 7.04 (SO_2O), 7.5–8.5 (CF, SO_2) μm; ^{1}H NMR 4.26 (s, OCH_3) ppm; ^{19}F NMR −75.0 (t, J_{FF} = 8.1 Hz, 3 F, CF_3), −106.8 (q, J_{FF} = 8.1 Hz, 2 F, CF_2) ppm.

Anal. Calcd for $C_4H_3F_5O_4S$: C, 19.84; H, 1.25; F, 39.24; S, 13.24. Found: C, 19.99; H, 1.40; F, 39.22; S, 12.85.

2-Hydroxy-2-phenylpentafluoropropanesulfonic Acid (11) and Its Pyridinium Salt. Ten milliliters of benzene was added to 9.8 g (0.043 mol) of 1 and the two-phase system was stirred at 25 °C. After 1 h, the mixture was homogeneous and was allowed to stand overnight. Evaporation of volatiles left a viscous residue of 11 which slowly crystallized to a deliquescent solid, mp 80–88 °C. IR analysis indicated the presence of SOH and C_6H_5 but not C═O.

The solid was dissolved in 25 mL of water and basified with 4.0 g (0.05 mol) of pyridine. Dilution to 50 mL with water and chilling to 0 °C precipitated 9.9 g of the pyridinium salt of 11, mp 110–113 °C. A second crop, 2.1 g, mp 110–113 °C, raised the yield to 12.0 g (73%). An analytical sample, mp 113.5–114.5 °C, was prepared by two recrystallizations from water: IR (KBr) 2.89, 3.08, 3.14, 3.23, 3.35, and 3.43 (OH, ═CH, NH^+), 6.12, 6.21, 6.50, and 6.70 (aromatic C═C, C═N, NH^+), 8–10 (CF, COH, SO_2) μm; ^{1}H NMR [$(CD_3)_2CO$] 6.2–8 (multiplets, OH, aromatic CH, NH^+) ppm; ^{19}F NMR −72.1 (d, J_{FF} = 12.1 Hz, into d, J_{FF} = 9.6 Hz, 3 F, CF_3) ppm with the strong central groups of an AB at −10 172 Hz (q, J_{FF} = 9.6 Hz, into m, 1 F, CF) and −10 200 Hz (q, J_{FF} = 12.1 Hz, into m, 1 F, CF).

Anal. Calcd for $C_{14}H_{12}NO_4F_5S$: C, 43.64; H, 3.14; N, 3.64; S, 8.23. Found: C, 43.80; H, 3.24; N, 3.55; S, 8.39.

2-Hydroxy-2-(phenoxyphenyl)pentafluoropropanesulfonic Acid (12) and Its Sodium Salt. A mixture of 9.0 g (0.0395 mol) of sulfonic acid 1 and 50 mL of diphenyl ether was stirred at 25 °C for 3 days. Addition of 3.5 g (0.044 mol) of pyridine caused separation of a water-soluble layer from which the pyridinium salt could not be crystallized. The heavy oil from evaporation of aqueous extracts was stirred with 1.6 g (0.04 mol) of NaOH. The solution was evaporated to low volume, absolute ethanol was added, and evaporation was continued to near dryness. The residue was stirred with 100 mL of absolute ethanol, carbonated with solid carbon dioxide, and filtered. Evaporation of the filtrate gave an oily concentrate which was taken up in 100 mL of ether and filtered, and the filtrate was evaporated to dryness. Addition of petroleum ether and scratching induced crystallization. Continuous extraction of the solid with ether slowly gave first a small amount of mixed solids and then 4.9 g (29%) of the sodium salt of **12**: mp 211–218 °C; IR (KBr) 2.85 (OH), 3.24 (unsaturated CH), 6.18, 6.27, 6.60, and 6.69 (aromatic C═C), 8–10 (CF, CO, SO_2O) μm; ^{1}H NMR (Me_2SO-d_6) 6.8–7.8 (m, 9 H, aromatic CH), 3.32 (s, 2 H with partial exchange into solvent, OH) ppm; ^{19}F NMR −71.5 (d, J_{FF} = 11.6 Hz, into d, J_{FF} = 10.0 Hz, 3 F, CF_3) with center lines of AB for CF_2 at −10 214 Hz (q, J_{FF} = 10.0 Hz, ~1 F) and −10 243 Hz (q, J_{FF} = 11.6 Hz, ~1 F).

Anal. Calcd for $C_{15}H_{10}F_5NaO_5S\cdot{}^1/_2H_2O$: C, 41.96; H, 2.58; F, 22.13; Na, 5.35. Found: C, 41.77; H, 2.61; F, 22.36; Na, 4.31.

2,2-Bis(*p*-hydroxyphenyl)pentafluoropropanesulfonic Acid (13) and Its Pyridinium Salt. When stirred under nitrogen, a mixture of 9.4 g (0.10 mol) of phenol and 9.0 g (0.0395 mol) of sulfonic acid 1 warmed spontaneously, darkened, and thickened. The mixture was heated and stirred at 100 °C under nitrogen for 3 h, after which time the reaction mixture had solidified. It was cooled, treated with 20 mL of water and 4.0 g (0.05 mol) of pyridine, and stirred until neutralization was complete. The heavy lower layer, nearly water insoluble, was isolated as a glass after volatiles were removed at 40 °C (0.5 mm). Crystallization was induced by prolonged contact with ether; mp 125–147 °C. Recrystallization from acetone/ether gave crops, mp 105–125 °C, 10.3 g (~55%), of the pyridinium salt of **13** containing some ether detectable by ^{1}H NMR. Prolonged evacuation at 100 °C converted the transparent crystals to an unsolvated white solid: mp 189–190 °C; IR (KBr) 3.0 (br, OH), 3.24 (unsaturated CH), 3.5–4 (NH^+, br), 6.19, 6.27, 6.58, and 6.72 (aromatic C=C and C=N), 8–9 (CF, CO, SO_2O), 12.17 (para-disubstituted aromatic), 13.35 and 14.75 (pyr ring) μm; ^{1}H NMR (acetone-d_6) 6.1 (br, 2 H, OH), 4.5–5.4 (m, 6 H, pyridinium ion) ppm, with AA′BB′ at 348, 339.5, 306, and 297.5 Hz (8 H, phenol CH); ^{19}F NMR −60.6 (t, J_{FF} = 13.3 Hz, 3 F, CF_3), −91.0 (q, J_{FF} = 13.3 Hz, 2 F, CF_2) ppm.

Anal. Calcd for $C_{20}H_{16}F_5NO_5S$: C, 50.32; H, 3.38; N, 2.93; S, 6.72. Found: C, 50.26; H, 3.33; N, 2.70; S, 6.75.

Copolymerization of 1 with Tetrafluoroethylene. Copolymerizations carried out under 100–400-psi, 500-atm, and 3000-atm pressure at 10–30 °C gave increasing incorporation of **1** with increasing pressure up to 1–2% **1** in the copolymer. Incorporation of **1** was below 1% at low pressures of tetrafluoroethylene, but the presence of a significant amount of **1** was established by the use of the acidic residues as dye sites. Treatment of the copolymers with a basic dye (Sevron Red GL) dissolved in ethanol/water gave orange-red polymers after exhaustive solvent extraction, whereas a poly(tetrafluoroethylene) control remained virtually colorless after treatment. The intensity of color increased in correspondence with the pressure under which the copolymerization was carried out.

A mixture of 22.8 g (0.10 mol) of **1**, 1.0 mL of 8% perfluoropropionyl peroxide initiator in 1,1,2-trichlorotrifluoroethane, and 40 mL of 1,1,2-trichlorotrifluoroethane was kept at 0 °C or less until charged into a 125-mL stainless-steel-lined tube. The tube was then cooled at −50 °C while 20 g (0.20 mol) of tetrafluoroethylene was added. Nitrogen pressure (2500 atm) was applied, and the mixture was warmed over 1 h to 30 °C and held there for 4 h. The resulting polymer was rinsed well with 1,1,2-trichlorotrifluoroethane, extracted with water, and dried at 100 °C (0.5 mm) leaving 13.9 g (~70%) of copolymer. A sample of the dried polymer was stirred for 3 h with concentrated NH_4OH; a small amount of 1,1,2-trichlorotrifluoroethane was added to promote contact between the solid and the aqueous phase. The washed and dried polymer was analyzed; large samples were used to give definitive results. Assuming the comonomer to be $CF_3C(-O-)CF_2SO_2ONH_4$ units, the analyses for N (0.12, 0.15) correspond to an equivalent weight of 10 800 or 2.3% by weight incorporation of the ammonium sulfonate. The analyses for S (0.18, 0.10) correspond to an equivalent weight of 22 900 or 1.1% of comonomer.

Copolymerization of 4 with Vinylidene Fluoride. **4** readily copolymerizes with vinylidene fluoride. An 80-mL Hastalloy-lined tube was loaded with a cold mixture of 20 mL of 1,1,2-trichlorotrifluoroethane, 5 mL of 8% perfluoropropionyl peroxide initiator in 1,1,2-trichlorotrifluoroethane, and 10.9 g (0.037 mol) of **4**. The tube was closed, cooled, and charged at −40 °C with 20 g (0.32 mol) of vinylidene fluoride. It was then shaken at 25 °C for 20 h. The reaction mixture was evaporated to 25 °C (<0.5 mm), leaving 25.8 g (ca. 83%) of solid copolymer. A sample of polymer was stirred with 250 mL of water for 4 h, isolated, and dried at 25 °C under vacuum. IR analysis showed broadened bands similar to those of poly(vinylidene fluoride) with added absorptions present; a medium-intensity band at 5.6 μm indicates some $C{=}CF_2$ or C=O present of unknown origin.

Anal. Calcd for 8.5:1 vinylidene fluoride/**4** copolymer: C, 31.59; H, 2.41; S, 3.83. Found: C, 31.79; H, 2.60; S, 3.93.

The sulfur analysis corresponds to an equivalent weight of 816 or a copolymer 36% by weight of **4**.

The dyeability of the copolymer with Sevron Red GL dye was tested in the same manner as described for the TFE/**1** copolymers above. The vinylidene fluoride/**4** copolymer after hydrolysis dyed readily to a deeper shade of red-orange than the TFE copolymer.

Polymerizations carried out with a higher proportion of **4** present gave copolymers containing higher percentages of **4** and having solubility in 1,1,2-trichlorotrifluoroethane.

Addition of Hexafluoroacetone to Benzene Catalyzed by Trifluoromethanesulfonic Acid. An 800-mL metal tube charged with 40.0 g (0.51 mol) of benzene, 180 g (1.1 mol) of hexafluoroacetone, and 5 mL of trifluoromethanesulfonic acid was heated at 150–160 °C for 14 h, during which time the pressure dropped from 500 to 365 psi. The tube was cooled, gases were vented, and the liquid product mixture was stirred with 5.6 g of sodium bicarbonate, filtered, and distilled. There was thus obtained 99.6 g (80%) of α,α-bis(trifluoromethyl)benzyl alcohol (**10**), bp 64–67 °C (20 mm), and only a few grams of a higher boiling residue.

Benzoylation Catalyzed by $CF_2{=}CF_2$/1 Copolymer. A mixture of 6.15 g (ca. 0.006 equiv) of powdered copolymer (equiv wt ca. 11 000), 28.1 g (0.20 mol) of benzoyl chloride, and 60 mL of *p*-xylene was stirred at 140 °C for 2 days. Filtration gave 6.12 g of recovered catalyst; distillation of the filtrate gave 4.3 g (10%) of 2,5-dimethylbenzophenone, bp 94–96 °C (0.025 mm), identified by its IR spectrum.

Benzoylation Catalyzed by Nafion H Beads. Nafion perfluorosulfonic acid polymer in the acidic form was obtained by stirring the potassium salt of Nafion 511 with excess concentrated nitric acid and extracting the solid with distilled water until the extract was neutral. A 2-g sample of resulting hydrated sulfonic acid of Nafion (equiv wt 1100) was evacuated to constant weight (1.13 g). The catalyst was suspended in 28.1 g (0.20 mol) of benzoyl chloride and 60 mL of *p*-xylene, and the mixture was stirred and heated slowly. At 110 °C gas evolution was first noted. After 20 h at 110–115 °C, the temperature was raised to 135 °C for 8 h. Rapid evolution of HCl slowed greatly and the catalyst was black. Titration of acidic off-gases with NaOH indicated a 68% yield of HCl. The reaction mixture was decanted from the catalyst, and the catalyst was rinsed with a small amount of *p*-xylene. The combined organic liquids were washed with 200 mL of 5% NaOH and 2 × 100 mL of water, dried, and distilled to give 29.2 g (70%) of 2,5-dimethylbenzophenone, bp 95–100 °C (0.1 mm). The IR spectrum was identical with that of an authentic sample.

The catalyst residue retained its activity, as shown by another reaction with 28.1 g (0.20 mol) of benzoyl chloride and 60 mL of *p*-xylene. This mixture was heated and stirred at 130 °C for 6 h and then at 135–140 °C for 6 h. Titration showed an 85% yield of HCl. The reaction mixture was decanted from the catalyst, the catalyst was rinsed with a little *p*-xylene, and the combined organics were distilled directly to afford 36.7 g (87%) of 2,5-dimethylbenzophenone, bp 104–109 °C (0.2 mm), and <1 g of residual oil.

Repetition of the last reaction using the same catalyst residue for the third time gave 82% of HCl and 35.1 g (84%) of 2,5-dimethylbenzophenone.

A sample of Nafion flake in the sulfonyl fluoride form having an equivalent weight of 1790 was hydrolyzed by heating it at 90 °C for 10 h in a mixture of 26 g of potassium hydroxide, 57 mL of dimethyl sulfoxide, and 120 mL of water. The potassium salt so obtained was converted to the acid form by treatment with 10 N HCl and then washed well with water and dried under vacuum. The reaction of benzoyl chloride with *p*-xylene was repeated with 1.13 g (0.006 equiv) of Nafion H (EW 1790) as catalyst. Heating was carried out at 135–140 °C for 2 days. The reaction mixture was cooled and filtered, and the solid was rinsed with *p*-xylene and dried under vacuum to give 1.27 g of recovered catalyst.

The filtrate was washed with 500 mL of 5% sodium hydroxide and then 100 mL of water, dried over anhydrous calcium sulfate, filtered, and distilled to give 6.8 g (16%) of 2,5-dimethylbenzophenone, bp 90–93 °C (0.05 mm). The product was identified by its IR spectrum.

2,5-Dimethyl-4′-nitrobenzophenone. A mixture of 1.10 g (0.001 equiv) of Nafion H perfluorosulfonic acid polymer (equiv wt 1100), 37.1 g (0.20 mol) of *p*-nitrobenzoyl chloride, and 60 mL of *p*-xylene was stirred at 135–145 °C for 26 h. The catalyst, 1.50 g, was recovered by filtration, rinsed with hot *p*-xylene, and dried under vacuum. The filtrate was diluted with 300 mL of ether, extracted with 500 mL of 5% $NaHCO_3$ solution, washed with water, dried, and evaporated to give an oily residue which crystallized. Recrystallization from 95% ethanol gave 16.5 g (32%) of 2,5-dimethyl-4′-nitrobenzophenone, mp 82–83.5 °C. An analytical sample prepared by recrystallization from hexane consisted of cream-colored crystals: mp 82.5–83.5 °C; IR (Nujol) 6.01 (conjugated C=O) μm; ^{1}H NMR (acetone-d_6) 8.13 (AA′BB′, 4 H, aromatic CH), 7.27 (s, 2 H, aromatic CH), 7.18 (s, 1 H, aromatic

CH), 2.32 (s, 3 H, CH_3), 2.28 (s, 3 H, CH_3) ppm.

Anal. Calcd for $C_{15}H_{13}NO_3$: C, 70.58; H, 5.13; N, 5.49. Found: C, 70.31; H, 4.99; N, 5.55.

2,5-Dimethoxybenzophenone. A mixture of 1.10 g (0.001 equiv) of Nafion H perfluorosulfonic acid polymer, 28.1 g (0.20 mol) of benzoyl chloride, 27.6 g (0.20 mol) of 1,4-dimethoxybenzene, and 50 mL of *n*-octane was stirred at 80 °C. Very slow evolution of HCl and darkening of the catalyst showed reaction to be occurring. The mixture was heated at 90–100 °C for 7 h, during which time continuous slow evolution of HCl occurred. Heating was continued at 120 °C for 5 h, where the initial moderate rate of HCl evolution became very slow near the end. The mixture was refluxed (132 °C) for 15 min, where very slow evolution of HCl indicated reaction had been completed. Filtration afforded 1.26 g of catalyst, and distillation of the filtrate gave 26.5 g (55%) of 2,5-dimethoxybenzophenone: bp 143–144 °C (0.1 mm); IR (neat) 3.25–3.52 (aromatic + saturated CH), 6.00 (conjugated C=O), 6.24, 6.30, and 6.71 (aromatic C=C μm; ^{1}H NMR (CCl_4) 6.9–7.8 (m, 8 H, aromatic CH), 3.64 (s, 3 H, OCH_3), 3.50 (s, 3 H, OCH_3) ppm.

The product crystallized on standing to form practically colorless crystals, mp 50–51 °C. Bogert and Howells[13] used aluminum chloride catalyst to prepare 2,5-dimethoxybenzophenone, mp 51 °C, in only 40% yield.

4-Chloro-4′-ethylbenzophenone. A mixture of 1.10 g (0.001 equiv) of Nafion H perfluorosulfonic acid polymer, 35.0 g (0.20 mol) of *p*-chlorobenzoyl chloride, and 60 mL of ethylbenzene was stirred at 105 °C for 3 days (slow evolution of HCl). When the mixture was heated at 145 °C for 1 h, only a small amount of HCl was evolved, indicating the reaction was nearly complete at 105 °C. Filtration and evaporation of the filtrate gave 50.3 g of a nearly solid residue. Two recrystallizations from methanol gave a first crop of 8.4 g, mp 85–88 °C, and a second crop of 2.3 g, mp 82–85 °C, for a total of 10.7 g (22%) of 4-chloro-4′-ethylbenzophenone. High-purity product, mp 92–92.5 °C, was obtained by one recrystallization from hexane. An analytical sample, mp 91.5–92.5 °C, was prepared by sublimation at 90 °C (0.05 mm): IR (CCl_4) 3.26 and 3.30 (aromatic CH), 3.36, 3.41, 3.47 (saturated CH), 6.01 (conjugated C=O), 6.21, 6.28, and 6.73 (aromatic C=C) μm; ^{1}H NMR (CCl_4) 7.8–7.2 (2 overlapping AA′BB′, 8 H, aromatic CH), 2.73 (q, J_{HH} = 7.6 Hz, 2 H, CH_2), 1.29 (t, J_{HH} = 7.6 Hz, 3 H, CH_3) ppm.

Anal. Calcd for $C_{15}H_{13}ClO$: C, 73.62; H, 5.35. Found: C, 73.88; H, 5.32.

The methanol filtrates from recrystallization of the crude product were diluted with a small amount of water to cause separation of a heavy oil. After removal of volatiles at 25 °C (0.05 mm), this oil weighed 18.6 g. IR and NMR analyses indicated a roughly equimolar mixture of 4-chloro-4′-ethylbenzophenone and 4-chloro-2′-ethylbenzophenone with lesser amounts of impurities such as methyl *p*-chlorobenzoate present.

1-Hydroxy-2-propionaphthone. A mixture of 11.0 g (0.01 equiv) of Nafion H perfluorosulfonic acid polymer, 28.6 g (0.22 mol) of propionic anhydride, 28.8 g (0.20 mol) of 1-naphthol, and 25 mL of *n*-octane was stirred overnight at reflux (132 °C) under nitrogen. The mixture was filtered hot, and the catalyst was rinsed with hot *n*-octane. The filtrate and rinsings were cooled at 0 °C to precipitate product, mp 83–85 °C. Recrystallization from 95% ethanol gave 29.2 g (73%) of yellow crystals, mp 84–85 °C [lit.[14] mp 81 °C]; IR (Nujol) 6.18 (chelated C=O) μm; ^{1}H NMR (acetone-d_6) 14.3 (s, 1 H, chelated OH), 8.0–6.7 (m, 6 H, aromatic CH), 2.62 (q, J_{HH} = 7.2 Hz, 2 H, CH_2), 0.70 (t, J_{HH} = 7.2 Hz, 3 H, CH_3) ppm.

Catalysis of Phthaloylation Reactions. While attempted condensations of phthaloyl chloride with *p*-xylene and with ethylbenzene at 140–145 °C gave black reaction mixtures indicative of side reactions, phthalic anhydride and *p*-xylene at 110–145 °C led mainly to recovery of phthalic acid after water workups, with 0.5% of 1,4-dimethylanthraquinone obtained as yellow-orange crystals, mp 138 °C. The ^{1}H NMR spectrum in C_6D_6 fits the assigned structure. In this case, the reaction mixture retained a light color, while the catalyst darkened at 90–100 °C. Although the catalyst may have been inactivated by coordination to 1,4-dimethylanthraquinone as its concentration increased, it retained its essential activity as demonstrated by its ability to catalyze the condensation of benzoyl chloride with *p*-xylene in a subsequent reaction.

Ethylation Catalyzed by Nafion. A 360-mL metal tube was charged with 3.35 g of a catalyst of Nafion perfluorosulfonic acid polymer (activated by reaction with PhCOCl) and 150 mL of *p*-xylene and then pressured to 750 psi at 25 °C with ethene. The tube was heated at 180 °C for 8 h, during which time ethene pressure was added as needed to maintain 1700 psi (total of 1.5 mol of ethene). The organic liquid was decanted and distilled to give fractions containing the mono-, di-, and triethyl derivatives in amounts estimated by GC analysis to be 28.6 g (14%) of the monoethyl derivative, 17.0 g (14%) of a mixture of the three diethyl derivatives, and 10.7 g (11%) of the triethyl derivative. The residue and last distillation cut contained 38.3 g (47%) of the crude tetraethyl derivative, largely crystalline. Two recrystallizations from ethanol gave purified isomer, mp 111–112 °C,[15] identified by ^{1}H NMR as the symmetrical 1,4-dimethyltetraethylbenzene.

Registry No. **1**, 53841-62-6; **1** tetrafluoroethylene copolymer, 71332-06-4; **2**, 62949-68-2; **3**, 71766-47-7; **4**, 67641-29-6; **4** vinylidene fluoride copolymer, 71332-04-2; **5**, 71766-48-8; **9**, 71766-49-9; **10**, 718-64-9; **11**, 71766-50-2; **11** pyridinium salt, 71766-51-3; **12**, 71766-52-4; **12** Na salt, 71766-53-5; **13**, 71766-54-6; **13** pyridinium salt, 71766-55-7; tetrafluoroethylene, 116-14-3; vinylidene fluoride, 75-38-7; trifluoroacetic acid, 76-05-1; ethyl pentafluoroisopropenyl ether, 2247-94-1; methyl trifluorovinyl ether, 3823-94-7; benzene, 71-43-2; diphenyl ether, 101-84-8; phenol, 108-95-2; hexafluoroacetone, 684-16-2; benzoyl chloride, 98-88-4; *p*-xylene, 106-42-3; 2,5-dimethylbenzophenone, 4044-60-4; 2,5-dimethyl-4′-nitrobenzophenone, 52137-58-3; *p*-nitrobenzoyl chloride, 122-04-3; 2,5-dimethoxybenzophenone, 4038-13-5; 1,4-dimethoxybenzene, 150-78-7; 4-chloro-4′-ethylbenzophenone, 71766-56-8; *p*-chlorobenzoyl chloride, 122-01-0; ethylbenzene, 100-41-4; 1-hydroxy-2-propionaphthone, 24490-31-1; propionic anhydride, 123-62-6; 1-naphthol, 90-15-3; phthaloyl chloride, 88-95-9; 1,4-dimethylanthraquinone, 1519-36-4; ethene, 74-85-1; 2-ethyl-1,4-dimethylbenzene, 1758-88-9; 2,3-diethyl-1,4-dimethylbenzene, 71766-57-9; 1,3-diethyl-2,5-dimethylbenzene, 71766-58-0; 1,4-diethyl-2,5-dimethylbenzene, 39144-22-4; 1,3,4-triethyl-2,5-dimethylbenzene, 71766-59-1; 1,2,4,5-tetraethyl-3,6-dimethylbenzene, 71766-60-4.

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[14] A. Hantzsch, *Ber. Chem. Dtsch. Ges.*, **39**, 3096 (1906).

[15] *Chem. Abstr.*, **71**, 322 (1969). A melting point of 109–110 °C is reported for a compound which appears to be 1,4-dimethyltetraethylbenzene.