The similarity in structure and patterns of reactivity of the neutral Rh(DO)(DOH)pn and the anionic "supernucleophiles" of Co(I) and Rh(I) make one wonder if the mechanistic pathways are not similar, and if so do those pathways extend to other metal centers.

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Synthesis of Hemifluorinated Ketones Using Disodium Tetracarbonylferrate(− II)

Sir:

Although hemifluorinated ketones, RCOR', where R is a simple alkyl or aryl and R' is a perfluorinated alkyl or aryl, can be prepared by several methods,[1-12] none of these procedures lend themselves to the preparation of such ketones in which R bears a functional group. We wish to report simple, single-flask syntheses of these hemifluorinated ketones using Na_2-$Fe(CO)_4$, an inexpensive transition metal reagent. These methods give good to excellent yields and can be employed in cases in which the hydrocarbon group R possesses unmasked nitrile, ester, or chloro groups.[13]

Earlier we employed $Na_2Fe(CO)_4$ to prepare unsymmetrical ketones[15,16] by sequentially adding two different aliphatic halides or sulfonates (eq 1 and 2). These *in situ* ketone syntheses were shown to go through either acyl or alkyl iron(0) intermediates **1** or **2** which have been isolated as their $[(Ph_3P)_2N^+]$ salts.[18] Our attempts to extend the procedures shown in eq 1 and 2 to the preparation of hemifluorinated ketones using perfluoroalkyl halides failed to give appreciable yields (Table I,

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(2) K. T. Dishart and R. Levine, *ibid.*, **78**, 2268 (1956).

(3) R. Fuchs and G. J. Park, *J. Org. Chem.*, **22**, 993 (1957).

(4) E. T. McBee, O. R. Pierce, and D. D. Meyer, *J. Amer. Chem. Soc.*, **77**, 917 (1955).

(5) A. Sykes, J. C. Tatlow, and C. R. Thomas, *J. Chem. Soc.*, 835 (1956).

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(10) D. A. Rausch, A. M. Lovelace, and L. E. Coleman, *J. Org. Chem.*, **21**, 1328 (1956).

(11) T. F. McGrath and R. Levine, *J. Amer. Chem. Soc.*, **77**, 3656 (1955).

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(13) Based on our experience using $Na_2Fe(CO)_4$ to prepare carboxylic acid derivatives,[14] ketones are also not usually attacked by this reagent.

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(15) J. P. Collman, S. R. Winter, and D. R. Clark, *ibid.*, **94**, 1788 (1972).

(16) Tsutsumi and coworkers[17] obtained moderate yields of unsymmetrical ketones by treating lithium acylferrates with acid chlorides and benzyl halides.

(17) (a) I. Rhee, M. Ryang, and S. Tsutsumi, *J. Organometal. Chem.*, **9**, 361 (1967); (b) Y. Sawa, M. Ryang, and S. Tsutsumi, *Tetrahedron Lett.*, 5189 (1960); (c) Y. Sawa, M. Ryang, and S. Tsutsumi, *J. Org. Chem.*, **35**, 4183 (1970).

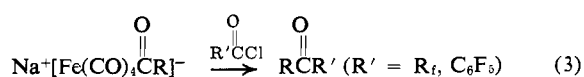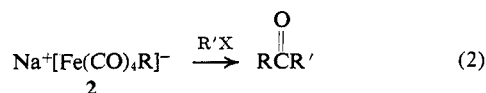(18) W. O. Siegl and J. P. Collman, *J. Amer. Chem. Soc.*, **94**, 2516 (1972).

a). This failure is probably caused by the reversed polarities of perfluoroalkyl halides,[19] $R_f^{\delta -}-X^{\delta +}$. Metal carbonyl anions have been reported to react with perfluoroalkyl iodides apparently through attack at iodine affording products of the type shown in eq 5.[20-23]

On the other hand, we have successfully used perfluoro acid chlorides, anhydrides, and pentafluorophenyl iodide to prepare these hemifluorinated ketones (Table I). For example, the method shown in eq 1 may be used by first introducing the perfluoroacyl group with the corresponding acid chloride and then adding an alkylating agent (Table I, g). However, this procedure is limited to very reactive alkylating reagents such as benzyl halides in the second step. Pentafluorophenyl iodide as the second reagent (R'X) gives good yields in the method shown in eq 1 (example b) but poor yields by that of eq 2 (d). Nonfluorinated aromatic iodides afford very low yields by method 1.

Earlier we found the methods outlined in eq 3 and 4 to give very low yields of ketones when ordinary aliphatic acid chlorides or anhydrides are employed as the second reagent.[24] However, perfluoroacyl chlorides (and anhydrides) afford good to excellent yields of hemifluorinated ketones by these methods (Table I). These procedures have all of the versatility of our earlier methods for the *in situ* generation of acyl and alkyl iron intermediates (**1** and **2**), starting from aliphatic halides and tosylates or acid chlorides and making use of the dramatic solvent effects manifested by these reactions.[25] Furthermore, unmasked functionality can be present in the nonfluorinated group R as illustrated by examples e, k, l, m, and o.

All of the compounds listed in Table I have been isolated and characterized by elemental analyses, pmr, and ir. We have demonstrated that the ketone in example h is formed *in situ* at 25° and not in the work-up by removing the product, n-$C_8H_{17}COC_3F_7$, from the mixture at reduced pressure. A typical procedure (m) is illustrated by synthesis of n-$C_7F_{15}COC_6H_{12}CN$ using eq 3. Into a slurry of $Na_2Fe(CO)_4$ (867 mg, 4.0 mmol) in 25 ml of THF at 25° under N_2 was injected $Br(CH_2)_6$-CN (0.56 ml, 3.6 mmol). The flask was flushed with CO and stirred under 5 psi for 5 hr, after which n-C_7-$F_{15}COCl$ (1.14 ml, 4.60 mmol) was injected. The mixture was stirred for 8 hr and then treated with acidified brine and extracted twice with ether. The organic layer was dried and concentrated to an oil which was chromatographed on silica with hexane. Removal of hexane and bulb-to-bulb distillation afforded 1.32 g (72%) of n-$C_7F_{15}COCH_2(CH_2)_4CH_2CN$ as a colorless liquid.

The different course that these reactions take with perfluoroacyl and pentafluorophenyl halides compared with hydrocarbon analogs (reactions 3 and 4 affording high yields with the former and low yields with the latter) is not understood. However, these

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(24) S. R. Winter, N. W. Hoffman, and J. P. Collman, unpublished results.

(25) J. P. Collman, J. N. Cawse, and J. I. Brauman, *J. Amer. Chem. Soc.*, **94**, 5905 (1972).

Table I. Hemifluorinated Ketones

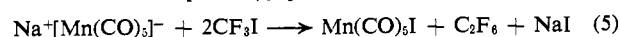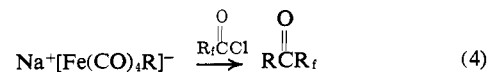|	First alkylating/ acylating reagent	Second alkylating/ acylating reagent	Method	Product	% overall[a] yield
a	n-$C_8H_{17}Br$	n-$C_7F_{15}I$	eq 1	n-$C_7F_{15}C(=O)\diagup\diagdown\diagup\diagdown\diagup$	12
b	n-$C_8H_{17}Br$	C_6F_5I	eq 1	$\diagup\diagdown\diagup\diagdown CC_6F_5$ (C=O)	59
c	n-$C_8H_{17}Br$	C_6F_5Br	eq 1	$\diagup\diagdown\diagup\diagdown CC_6F_5$ (C=O)	28
d	n-$C_8H_{17}Br$	C_6F_5I	eq 2	$\diagdown\diagup\diagdown\diagup CC_6F_5$ (C=O)	9
e	$\diagup\diagdown\diagup\overset{O}{\underset{O}{C}}\diagdown\diagup\diagdown Br$	C_6F_5I	eq 2	$\diagup\diagdown\diagup\overset{O}{\underset{O}{C}}\diagdown\diagup\diagdown CC_6F_5$ (C=O)	65
f	2-$C_8H_{17}OTs$	C_6F_5I	eq 1	$\diagup\diagdown\diagup\diagdown CC_6F_5$ (C=O)	57 (52[b])
g	n-$C_7F_{15}\overset{O}{C}Cl$	$C_6H_5CH_2Br$	eq 1	n-$C_7F_{15}\overset{O}{C}CH_2C_6H_5$	59
h	n-$C_8H_{17}Br$	$(n$-$C_3F_7\overset{O}{C})_2O$	eq 4	n-$C_3F_7\overset{O}{C}\diagup\diagdown\diagup\diagdown$	75
i	$C_6H_5\overset{O}{C}Cl$	n-$C_7F_{15}\overset{O}{C}Cl$	eq 3	n-$C_7F_{15}\overset{O}{C}C_6H_5$	76
j	$C_6H_5CH_2COCl$	n-$C_7F_{15}\overset{O}{C}Cl$	eq 3	n-$C_7F_{15}\overset{O}{C}CH_2C_6H_5$	70
k	$Cl\diagup\diagdown\diagup\diagdown Br$	n-$C_7F_{15}\overset{O}{C}Cl$	eq 3	n-$C_7F_{15}\overset{O}{C}\diagup\diagdown\diagup\diagdown Cl$	76
l	$\diagup\diagdown\diagup\overset{O}{\underset{O}{C}}\diagdown\diagup\diagdown Br$	n-$C_7F_{15}\overset{O}{C}Cl$	eq 4	n-$C_7F_{15}\overset{O}{C}\diagup\diagdown\diagup\diagdown\overset{O}{\underset{O}{C}}\diagdown\diagup$	90 (78[b])
m	$NC\diagup\diagdown\diagup\diagdown Br$	n-$C_7F_{15}\overset{O}{C}Cl$	eq 3	n-$C_7F_{15}\overset{O}{C}\diagup\diagdown\diagup\diagdown CN$	72[b]
n	$\diagup\diagdown\diagup\diagdown Br$	$C_6F_5\overset{O}{C}Cl$	eq 3	$C_6F_5\overset{O}{C}\diagup\diagdown\diagup\diagdown$	99
o	$\diagup\diagdown\diagup O\overset{}{\underset{O}{C}}\diagdown\diagup\diagdown Br$	$C_6F_5\overset{O}{C}Cl$	eq 3	$C_6F_5\overset{O}{C}\diagup\diagdown\diagup\diagdown\overset{}{\underset{O}{C}}O\diagdown\diagup$	71
p	$\diagup\diagdown\diagup\diagdown_{OTs}$	$C_6F_5\overset{O}{C}Cl$	eq 3	$C_6F_5\overset{O}{C}\diagup\diagdown\diagup\diagdown$	72

[a] Glc yield ($\pm3\%$) using internal standards. [b] Isolated yield.

differences may be due to a change in the site of attack (iron *vs.* acyl oxygen) by the less polarizable perfluoroderivatives and/or the greater tendency of the perfluoroacyl derivatives to undergo decarbonylation (reverse migratory insertion). This matter is currently being investigated by examining the intermediates formed in these reactions at low temperatures.
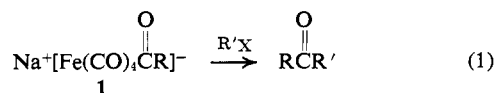
$$Na^+[Fe(CO)_4\overset{O}{C}R]^- \xrightarrow{R'X} R\overset{O}{C}R' \quad (1)$$
$$\mathbf{1}$$

$$Na^+[Fe(CO)_4R]^- \xrightarrow{R'X} R\overset{O}{C}R' \quad (2)$$
$$\mathbf{2}$$

$$Na^+[Fe(CO)_4\overset{O}{C}R]^- \xrightarrow{R'\overset{O}{C}Cl} R\overset{O}{C}R' \ (R' = R_f, C_6F_5) \quad (3)$$

$$Na^+[Fe(CO)_4R]^- \xrightarrow{R_f\overset{O}{C}Cl} R\overset{O}{C}R_f \quad (4)$$

$$Na^+[Mn(CO)_5]^- + 2CF_3I \longrightarrow Mn(CO)_5I + C_2F_6 + NaI \quad (5)$$

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Chiral, Hinged, and Functionalized Multiheteromacrocycles[1]

Sir:

The pioneering "Pedersen Papers"[2] on crown ether chemistry and the remarkable properties of Simmons and Park's *out–in* bicyclic amines[3] and of Lehn's cryptates[4] stimulated us to turn from the study of effects of crown ethers on ion-pair phenomena[5] to synthesizing multiheteromacrocycles with cavities shaped to complex selected species. Host cycles that exhibit properties of chiral recognition of potential guest molecules would be particularly interesting. This paper reports syntheses of crowns containing chiral steric barriers, some with transannularly located functionalized side chains.

Without high dilution, β,β'-dihydroxy-α,α'-binaphthyl (1), ditosylates of polyethylene glycols and potassium *tert*-butoxide[6a] in tetrahydrofuran[6b] (or sodium or potassium hydroxide in dioxane–butanol)[2a] gave cycles[7] 2, 3, and 4. Intermediate 5 treated under similar conditions with catechol (derivatives or analogs) gave 6–10. With Na₂S in butanol–dioxane, 5 gave 11. From catechol, 12 was prepared similarly to 5. From 12 and 1, 6 was synthesized (50%). Conventional reactions converted 9 to 13. Biphenylcrown 14 was prepared from *o,o'*-dihydroxybiphenyl and the dichloride of pentaethylene glycol.

All cycles tested (2, 3, 6, 13, and 14) dissolved in chloroform the otherwise insoluble *tert*-butylammonium tetraphenylborate. Complexation (1:1) produced marked chemical shifts and multiplicity changes of nmr spectral bands. The 1:1 complex[7a] of 2 crystallized (chloroform), mp 118–120° dec. Cycles 3 and 6 (only ones tested) dissolved hydronium tosylate (1 mol) in

Scheme I[a]

	n	%	Mp, °C
2,[7a]	4	45	107–108.5
3,[7]	5	60	130–130.5
4,[7a]	6	48	oil

	A	B	X	Y	%	Mp, °C
6,[7]	O	O	H	H	41	147–148
7,[7]	S	S	H	H	72	149–150
8,[7]	O	S	H	H	38	111–113
9,[7]	O	O	CH=CHCH₃	H	41	oil
10,[7]	O	O	H	(CH₂)₃OH	16	oil

11,[7] 53%, mp 127–128°   **12**,[7a] 48%, oil   **14**,[7] 12%, mp 64–65°

13,[7] 36%, mp 193–194°

[a] BN = β,β'-substituted α,α'-binaphthyl; BP = 2,2'-substituted biphenyl.

chloroform by complexation. Similarly, 3 dissolved potassium permanganate in benzene.[8] Tetrabutylammonium hydroxide when substituted for metal bases reduced yields (factor ~2 to 3) in preparations of cycles 3 and 6. Apparently metal ion templating of open-chain starting material produced the higher yields.

Macroreticular resin[9a] was used to characterize the cycles' complexing power for cations at the resin–solvent interface.[9b] For each cation and cycle, the resin became saturated with cycle to an extent ($\pm 5\%$) independent of cycle concentration in dichloromethane, and $K_s = 100 \times$ (moles adsorbed cycle)/(moles cation present). For tribenzylamine against resin–H₃O⁺, $K_s = 18.6$. Values of K_s for resin–H₃O⁺, –Na⁺, –K⁺, –NH₄⁺, and –Cs⁺ complexing the cyclic ethers were respectively: benzo[15]crown-5,[2a] 1.3, 1.2, 0.69, 0.43, 0.19; benzo[18]crown-6,[2a] 3.6, 1.1, 1.3, 1.05, 0.69; dibenzo[18]crown-6,[2a] 1.35, 0.89, 0.97, 0.65, 0.40; 2, 0.40, 0.59, 0.21, 0.096, 0.027; 3, 0.91, 0.67, 0.57, 0.47, 0.23; 4, 0.92, 0.61, 0.49, 0.45, 0.29; 6, 0.54, 0.55, 0.43, 0.30, 0.095; 11, 0.95, 0.19, 0.029, 0.017, 0.000; 8, 0.83, 0.29, 0.13, 0.057, 0.007; 13, 1.14, 0.54, 0.31, 0.30, 0.047; 14, 1.4, 0.74, 0.56, 0.43, 0.19. The trends indicate: aromatic rings decrease K_s's; K_s for resin–H₃O⁺ > –Na⁺ > –K⁺ > –NH₄⁺ > –Cs⁺, except for 2 (–Na⁺ > –H₃O⁺) and for benzo- and dibenzo[18]crown-6 (–K⁺ > –Na⁺); six-oxygen cycles complex better than five; S substituted for O lowers K_s, except for resin–H₃O⁺; the side chain of 13 de-

(1) This work was supported by the U. S. Public Health Service Research Grant No. GM 12640-08 from the Department of Health, Education and Welfare, and by a grant from the National Science Foundation, GP 33533X.

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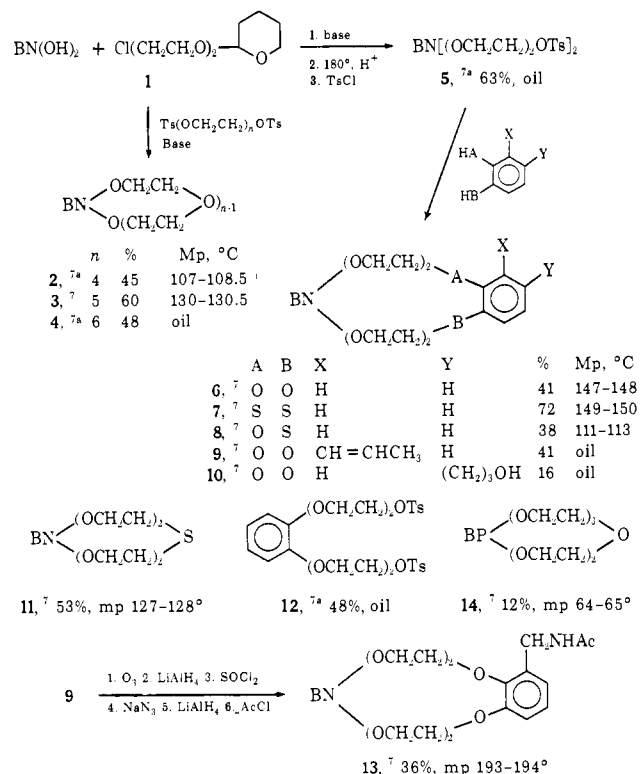
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(9) (a) Amberlyst-15, polystyrenesulfonic acid, Rohm and Haas, 40–60 mesh, average pore diameter, 200–600 Å. (b) Dry resin saturated with H₃O⁺, Na⁺, K⁺, NH₄⁺, or Cs⁺ (25–50 mg) was mixed with 5 to 12 × 10⁻⁵ M solution of cycle in dry dichloromethane. The solution's optical density (λ 250–340 nm) was measured before mixing and monitored until constant (mixture shaken at 25°).