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Reaction of chlorodifluoromethylketones with nickel carbonyl*

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Abstract

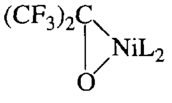
Carbon monoxide-containing complexes formed from nickel carbonyl and *F*-ketones in donor solvents are stable at 25 °C and decompose on heating with little or no elimination of fluoride ion. However, treatment of one such complex with iodobenzene at 25 °C resulted in benzoylation at oxygen with a concomitant loss of fluoride. Fluoroketones bearing an α-chlorine atom, on the other hand, reacted with nickel carbonyl at moderate temperatures with the facile loss of chloride ion to form, sequentially, enolate, keto alcohol, 1,6-diketone and cyclic diol derivatives. Methyl trifluoropyruvate has been shown to be a special case in which reductive dimerization to dimethyl 1,2-dihydroxy-1,2-bis(trifluoromethyl)succinate was induced by nickel carbonyl rather than simple complexation.

Introduction

The unusually high stability of complexes [1] formed between fluorinated ligands and lower valent transition metal derivatives generally mitigates against reactions catalyzed by transition metals. The use of equivalent amounts of inexpensive transition metal compounds as reagents to bring about new transformations of fluorinated substrates is therefore being pursued**. The results obtained with nickel carbonyl and some fluoroketones are presented here.

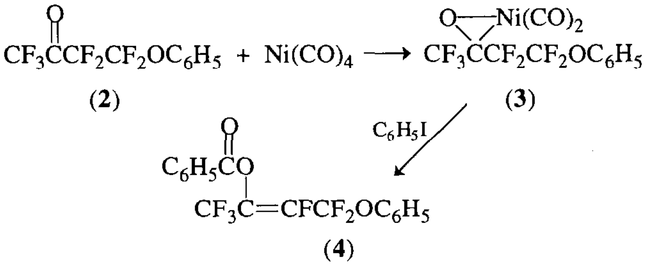
Results and discussion

Addition of hexafluoroacetone to various zerovalent nickel complexes has been shown previously to give adducts best described as the σ-bonded structures **1** [3]. Nickel carbonyl appears to form a similar adduct with hexafluoroacetone in dimethylformamide after the partial loss of carbon monoxide. The tightly bonded fluoroketone is not easily reacted or displaced, but GC analysis of a solution of the deep red complex from nickel carbonyl and hexafluoroacetone shows that the latter is regenerated on heating in the injector part while nickel carbonyl was not detected. The preformed complex is unreactive toward chloropentafluoroacetone at 25 °C and reacts sluggishly on warming to give a complex mixture of products, suggesting slight dissociation of hexafluoroacetone from the heated complex (*vide infra*).



(**1**)

Similarly, nickel carbonyl adds an equivalent 4-phenoxyheptafluorobutanone-2 (**2**) [4] in benzonitrile solvent to produce a soluble dark red complex. This complex appears to be stable at 80 °C, but also thermolyzes on a GC column to produce carbon monoxide and regenerated ketone. It reacted with iodobenzene to give the benzoylated enols **4** ($E/Z=10{:}1$), confirming the presence of at least one carbon monoxide molecule as a ligand and suggesting structure **3** for the complex.



(**4**)

The reaction is presumably initiated by the addition of iodobenzene to nickel, followed by insertion of carbon monoxide into the phenyl–nickel bond to form the benzoyl moiety. Subsequent benzoylation at oxygen to generate intermediate **5**, having transformed the organic

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*Contribution No. #6319.

**An account of work with iron pentacarbonyl has appeared earlier [2].

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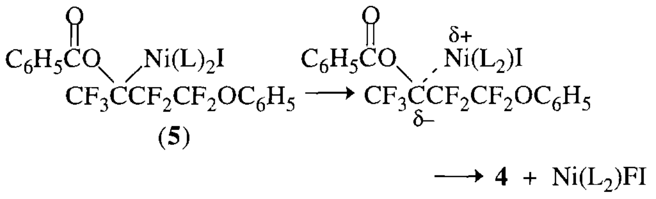
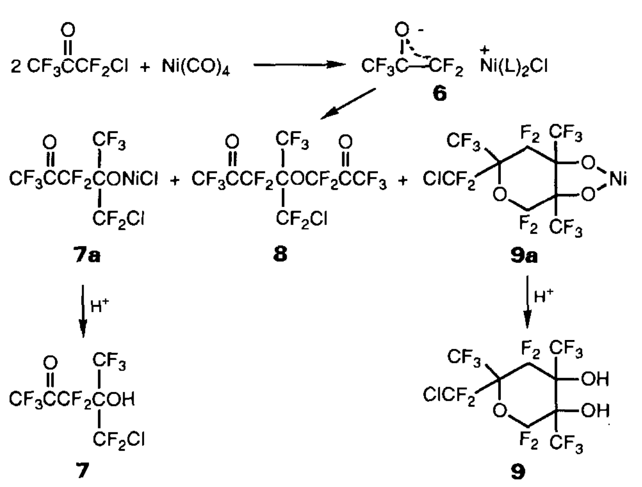
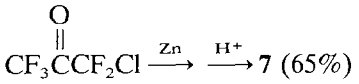
ligand into an ionizable group, facilitates the transfer of α-fluorine to nickel via a β-elimination of fluoride with the formation of **4**. Insertion of nickel carbonyl into a C—F bond to form the oxa-π-allyl (enolate) complex was considered as an alternative to the intermediacy of **3**. The absence of a subsequent enolate addition to another molecule of reactive fluoroketone, as observed in the α-chlorofluoroketone case, would seem to mitigate against such an insertion.



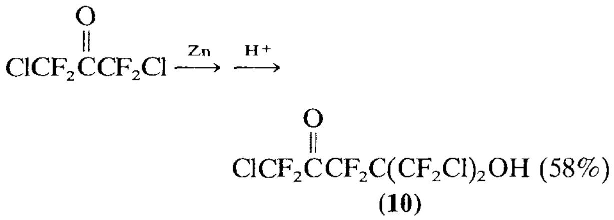
The early experiments described above demonstrated the reluctance with which Ni^0 complexes of fluoroketones bearing fluorine atoms as the only α-substituents form enolate salts by cleavage of a carbon–fluorine bond. This may be contrasted with the behavior observed when α-chlorine is present. Treatment of chloropentafluoroacetone with nickel carbonyl results in the ready cleavage of chloride from the intermediate complex to form a reactive intermediate presumed to be the nickel enolate **6**. Subsequent reactions of **6** as it is formed lead to the products **7–9**.



In agreement with the proposed sequential formation of **6–9**, the use of excess (3:1) chloropentafluoroacetone favored the formation of the early product **7**. Selective formation of the keto alcohol **7** was even better attained via the zinc-based enolate, since the secondary reactions observed with nickel (a transition metal) were avoided. In fact, although 1,3-dichlorotetrafluoroacetone tends to form low polymers with nickel carbonyl, it readily gives the keto alcohol **10** with zinc dust. The reagent Zn^0 also shows some promise in the preparation of mixed adducts such as **11** [5].

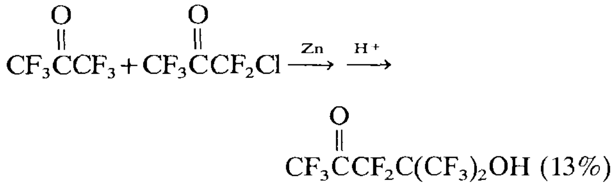


$$CF_3\overset{O}{\overset{\|}{C}}CF_2Cl \xrightarrow{Zn} \xrightarrow{H^+} \mathbf{7}\ (65\%)$$



$$ClCF_2\overset{O}{\overset{\|}{C}}CF_2Cl \xrightarrow{Zn} \xrightarrow{H^+} ClCF_2\overset{O}{\overset{\|}{C}}CF_2C(CF_2Cl)_2OH\ (58\%)$$

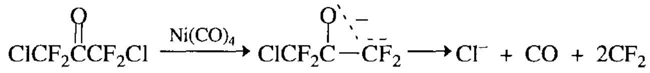
(10)



$$CF_3\overset{O}{\overset{\|}{C}}CF_3 + CF_3\overset{O}{\overset{\|}{C}}CF_2Cl \xrightarrow{Zn} \xrightarrow{H^+} CF_3\overset{O}{\overset{\|}{C}}CF_2C(CF_3)_2OH\ (13\%)$$

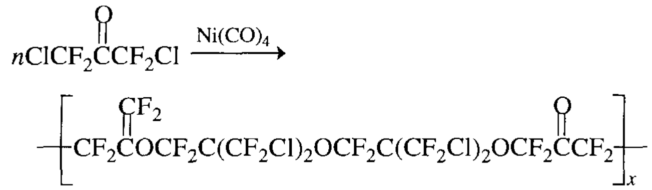
(11)

Elemental analysis of the insoluble product obtained from 1,3-dichlorotetrafluoroacetone indicated the presence of multiple CF_2 units in addition to the expected ketone and enolate units. A possible source of difluoromethylene is the fragmentation reaction of the intermediate nickel enolate with $NiCl_2$ and CO as stable by-products.



$$ClCF_2\overset{O}{\overset{\|}{C}}CF_2Cl \xrightarrow{Ni(CO)_4} ClCF_2\overset{O^-}{C}{=}CF_2 \longrightarrow Cl^- + CO + 2CF_2$$

The formation of adducts from anionic intermediates and difluoromethylene provides a means of incorporating CF_2 into the product. Structural elements believed to be present in the product are represented in the structure given below, and the empirical formula roughly approximates that determined by analysis.



$$n\,ClCF_2\overset{O}{\overset{\|}{C}}CF_2Cl \xrightarrow{Ni(CO)_4} \left[CF_2\overset{CF_2}{\overset{\|}{C}}OCF_2C(CF_2Cl)_2OCF_2C(CF_2Cl)_2OCF_2\overset{O}{\overset{\|}{C}}CF_2 \right]_x$$

Attempts to react the sodium salt or the nickel(II) salt of keto alcohol **7** with chloropentafluoroacetone to form **8** failed. This result was not unexpected, since such displacements of chloride with related fluoroalkoxides proceed only slowly on heating*. Hence, the mechanism proposed for effecting this condensation under the very mild conditions employed in the present work is formation of intermediate **8a** by ligand exchange followed by reductive elimination. The final stage of the reaction sequence, i.e. intramolecular reductive

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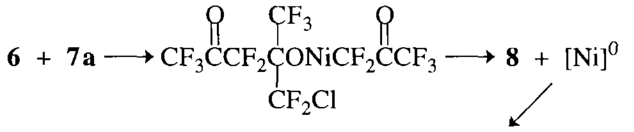
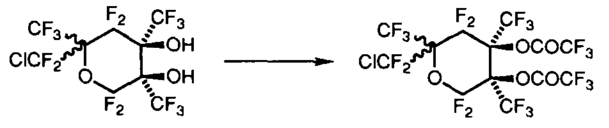
*The α-effect is operative in displacements of chlorine from α-chloroketones in highly fluorinated systems [6].

dimerization of **8** by Ni^0 to form **9a**, is apparently facile, since the yields of **8** were low relative to those of **9a**.



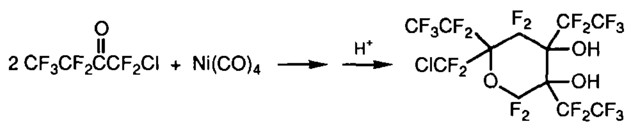
$$6 + 7a \longrightarrow CF_3\overset{O}{\overset{\|}{C}}CF_2\underset{CF_2Cl}{\overset{CF_3}{C}}ONiCF_2\overset{O}{\overset{\|}{C}}CF_3 \longrightarrow 8 + [Ni]^0 \qquad (8a) \qquad \swarrow 9a$$

When liberated from salts **9a** by acidification, glycol **9** proved to be a mixture of only two racemic pairs despite the presence of three chiral centers. In order to account for this observation, salt **9a** is depicted as having been formed with a small ring containing a single nickel atom and a presumed *cis* arrangement of the vicinal oxygen atoms. The two sets of diastereomers in **9** were identified by GC/MS and by NMR spectroscopy; in addition, trifluoroacetylation was shown by GC/MS to provide the corresponding bis(trifluoroacetates) **12**.



9 **12**

The cyclic pinacol synthesis could be extended to the next higher homolog, 1-chloroheptafluorobutanone-2. Again, two sets of diastereomers (**13**) were obtained.



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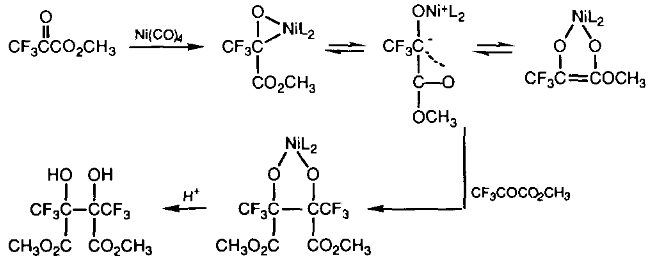
The presence of an α-ester group in the fluoroketone facilitates reaction beyond the simple complex stage, allowing isolation of the reductive dimerization product **14** as a meso and D/L mixture after acidification. Such glycol formation was not observed with either hexafluoroacetone or **2** and may be attributable to weakening of the C—Ni bond in the complex to allow insertion of a second carbonyl moiety. Reductive dimerization of methyl trifluoropyruvate to form glycol **14** occurs even more cleanly (62%) with zinc.



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Experimental

NMR spectra were taken on 20% solutions in $CDCl_3$ with $(CH_3)_4Si$ and $CFCl_3$ as internal references. ^{19}F NMR spectra were measured on a General Electric QE Plus instrument operating at 283.11 MHz and ^1H spectra were measured on a General Electric QE Plus instrument operating at 300.15 MHz.

Caution! Nickel carbonyl is well known as a highly toxic and volatile material that should be handled with extreme care in a hood.

E- *and Z-1-Phenoxy-3-benzoyloxyhexafluorobutene-2 (4)*

4-Phenoxyheptafluorobutanone-2 (**2**) (29.1 g, 0.10 mmol), 100 ml of benzonitrile and 8.5 g (0.05 mol, 6.5 ml) of nickel carbonyl were stirred under nitrogen at 70–80 °C when a soluble dark red complex formed over a 5-h period; subsequent heating at 80–90 °C for 15 h gave little change. Another 8.5 g (0.05 mol) of nickel carbonyl was added and reaction was continued at 80–85 °C for 4 h. GC analysis indicated the presence of considerable CO and regenerated starting ketone along with a minor amount of nickel carbonyl. The deep red solution was then reacted with 40.8 g (0.20 mol) of iodobenzene (added in two portions) at 75 °C for 8.5 h. Volatiles were removed by warming at 0.01 mmHg pressure, and the residual oil and solid were extracted with 2×200 ml of ether. The combined ether extracts were evaporated, the residual oil taken up in 50 ml of petroleum ether, filtered and fractionated to give 17.6 g (47%) of **4** ($E/Z = 10$), b.p. 92–93 °C/0.1 mmHg. IR (neat) (cm^{-1}): 3070 (arom. CH); 1770 (C=O); 1680 (C=C); 1600, 1490 and 1450 (arom. C=C); 1250–1150 (CF, C–O). ^1H NMR ($CDCl_3$) δ: 7.90 (m, 2H, arom. H *ortho* to C=O); 7.5–6.8 (m, 8H, remaining arom. CH) ppm. ^{19}F NMR for *E* isomer ϕ: −66.7 (d, $J_{FF} = 18$ Hz, 3F, CF_3); −71.3 (d, $J_{FF} = 9$ Hz, 2F, CF_2O); −136.3 (q of t, $J_{FF} = 18$, 9 Hz, 1F, =CF) ^{19}F NMR for *Z* isomer ϕ: −63.8 (q, $J_{FF} = 10$ Hz, 3F, CF_3); −69.6 (p, $J_{FF} = 10$ Hz, 2F, CF_2O); −123.7 (sextet, $J_{FF} = 10$ Hz, 1F, =CF) ppm. GC/MS (*E* isomer) *m/e*: 376 (M^+); 357 ($M^+ - F$); 106 ($C_6H_5CHO^+$); 105 ($C_6H_5CO^+$); 96 ($C_6H_5F^+$); 93 ($C_6H_5O^+$); 78 ($C_6H_6^+$); 77 ($C_6H_5^+$). The mass spectrum of the *Z* isomer was similar. Analysis: Calc. for $C_{17}H_{10}F_6O_3$: C, 54.27; H, 2.68%. Found: C, 54.51; H, 2.95%.

4-Chlorodifluoromethyl-2,2,5,5-tetrafluoro-1,4,6-tris(trifluoromethyl)-3-oxacyclohexane-diol-1,6 isomers (9) and their bis(trifluoroacetates) (12)

A mixture consisting of 26.2 g (20 ml, 0.15 mol) of nickel carbonyl, 250 ml of purified benzonitrile and 50 g (0.27 mol) of chloropentafluoroacetone was blanketed with nitrogen and stirred under a −80 °C condenser for 18 h while CO was evolved and a green solid precipitated. An additional 17.1 g (13 ml, 0.10 mol) of nickel carbonyl was added and reaction continued for 1 d further. After this time, gas evolution had nearly ceased and GC analysis indicated virtually complete consumption of both reactants. Another 50 g (0.27 mol) of chloropentafluoroacetone was added and the reaction continued for 2 d more. Removal of volatiles under vacuum gave a small amount of recovered chloropentafluoroacetone and benzonitrile solvent along with 15 g of a second layer which was indicated by GC/MS to be *c.* 50% diketone **8**; GC/MS *m/e*: 441 ($M^+ - Cl$); 413 ($M^+ - CO - Cl$); 391 ($M^+ - CF_2Cl$); 379 and 381 ($M^+ - CF_3CO$); 313 and 315 ($M^+ - CF_3COCF_2O$); 197 ($C_4F_7O^+$); 181 ($CF_2{=}C(CF_3)CF_2^+$); 147 ($CF_3COCF_2^+$); 119 ($C_2F_5^+$); 97 (CF_3CO^+); 85 and 87 (CF_2Cl^+); 78 (CF_2CO^+); 69 (CF_3^+). Pure **8** was subsequently isolated (*vide infra*).

The solid green residue was extracted with 200 ml of CH_2Cl_2 and the filtered extract evaporated to afford 57 g of dark green, stiff tar. Trituration of this residue with 50 ml of conc. H_2SO_4, extraction with 25 ml of $CFCl_2CF_2Cl$, clarification of the extract with $CaSO_4$ and fractionation gave 20.6 g [34% based on $Ni(CO)_4$] of mixed glycols **9**, b.p. 60–65 °C 3.6 mmHg, m.p. 43–70 °C and varying with distillation cut. IR ($CDCl_3$) (cm^{-1}): 3500 (OH); 1300–1100 (CF, C–O). ^1H NMR ($CDCl_3$) δ: 5.13 (s, 1H, OH); 4.20 (s, 1H, OH) ppm. ^{19}F NMR (for two racemates in *c.* equal amounts) ϕ: −50.1 (A branch d of m, $J_{FF} = 190$ Hz, 1F, CF_2Cl); −56.9 (B branch d of m, $J_{FF} = 190$ Hz, 1F, CF_2Cl and overlapping A branch d, $J_{FF} = 190$ Hz, 1F, CF_2Cl); −60.0 (B branch d, $J_{FF} = 190$ Hz, 1F, CF_2Cl); −66.0 (broad s, 3F, CF_3); −69.9 (m, 6F, CF_3); −70.3 (m, 3F, CF_3); −80.2 (t, $J_{FF} = 12$ Hz, 3F, CF_3); −80.4 (t, $J_{FF} = 12$ Hz, 3F, CF_3); −106.1 (A branch d of m, $J_{FF} = 280$ Hz, 1F, CF_2O); −107.7 (A branch d, $J_{FF} = 280$ Hz, 1F, CF_2O); −110.3 (B branch d, $J_{FF} = 280$ Hz, 1F, CF_2O); −111.0 (B branch d, $J_{FF} = 280$ Hz, 1F, CF_2O); −122.1 (A branch d of m, $J_{FF} = 275$ Hz, 1F, CF_2); −122.5 (A branch d of m, $J_{FF} = 275$ Hz, 1F, CF_2); −123.0 (B branch d of m, $J_{FF} = 275$ Hz, 2F, CF_2) ppm. GC/MS (two isomers in *c* equal amount and having very similar spectra) *m/e*; for one isomer: 441 and 443 ($M^+ - H_2O - F$); 425 ($M^+ - H_2O - Cl$); 409 and 411 ($M^+ - CF_3$); 391 and 393 ($M^+ - H_2O - CF_3$); 389 and 391 ($M^+ - HF - CF_3$); 375 ($M^+ - H_2O - CF_2Cl$); 373 ($M^+ - HF - CF_2Cl$); 247 ($C_5F_9O^+$); 197 ($C_4F_7O^+$); 181 ($CF_2{=}C(CF_3)CF_2^+$); 148 ($CF_3C(OH){=}CF_2^+$); 147 ($CF_3COCF_2^+$); 129 (CF_3COCHF^+); 128 (CF_3COCF^+); 109 ($C_3F_3O^+$); 100 ($C_2F_4^+$); 97 (CF_3CO^+); 85 and 87 (CF_2Cl^+); 78 (CF_2CO^+); 69 (CF_3^+); 51 (CF_2H^+); 50 (CF_2^+). Mass measured peaks were 424.9619 (calc. 424.9658 for $C_9F_{15}O$), 408.9542 (calc. 408.9500 for $C_8H_2ClF_{12}O_3$), 388.9418 (calc. 388.9438 for $C_8HO_3ClF_{11}$), 374.9712 (calc. 374.9690 for $C_8F_{13}O_2$) and 246.9718 (calc. 246.9805 for C_5F_9O). Analysis: Calc. for $C_9H_2ClF_{15}O_3$: C, 22.59; H, 0.42; Cl, 7.41; F, 59.55%. Found: C, 22.77; H, 0.46; Cl, 7.13; F, 59.97%.

Derivatization with $(CF_3CO)_2O$/pyridine produced the two isomeric bis(trifluoroacetates). GC/MS *m/e*: 651 and 653 ($M^+ - F$); 635 ($M^+ - Cl$); 441 and 443 ($M^+ - F - (CF_3CO)_2O$); 425 ($M^+ - Cl - (CF_3CO)_2O$) for one racemate and *m/e* 635 ($M^+ - Cl$); 425 ($M^+ - Cl - (CF_3CO)_2O$) for the other.

A change from nitrile solvent to THF essentially gave the same reaction sequence, but at a slower rate. The nickel salts formed were soluble in THF.

2-Chlorodifluoromethyl-4-keto-octafluoropentanol-2 (7) and 4-chlorodifluoromethyl-4-trifluoromethyl-2,6-diketodecafluoro-4-oxaoctane (8)

Reaction of excess chloropentafluoroacetone with nickel carbonyl (i.e. 3:1 mole ratio) favored the early product **7** rather than **9**. A mixture consisting of 60 g (0.33 mol) of chloropentafluoroacetone, 250 ml of purified benzonitrile and 13 ml (17.1 g, 0.10 mol) of nickel carbonyl was stirred in a nitrogen atmosphere under a −80 °C condenser while steady evolution of gas occurred. After 4 d, the mixture was distilled to dryness under vacuum, giving a mixture in the −80 °C trap identified as mainly CF_3COCF_2Cl and **8** by GC/MS analysis. Fractionation of these volatiles gave 4.2 g of **8** contaminated with benzonitrile, b.p. 65–66 °C/50 mmHg. Pure **8**, 3.6 g (8%), was obtained by transferring the distillate from conc. H_2SO_4 under high vacuum. IR (CCl_4) (cm^{-1}): 1810 (C=O); 1300–1100 (CF, C–O). ^1H NMR ($CDCl_3$) δ: none. ^{19}F NMR ϕ: −54.6 (m, 2F, CF_2Cl); −66.0 (septet, $J_{FF} = 12.3$ Hz, 3F, CF_3); −73.7 (m, 2F, OCF_2); −74.1 (t, $J_{FF} = 9.2$ Hz, 3F, $CF_3C{=}O$); −74.7 (t, $J_{FF} = 6.4$ Hz, 3F, $CF_3C{=}O$); −106.4 (A branch d of m, $J_{FF} = 297$ Hz, 1F, CF_2); −108.7 (B branch d of m, $J_{FF} = 297$ Hz, 1F, CF_2) ppm. Analysis: Calc. for $C_9ClF_{15}O_3$: C, 22.68; Cl, 7.44; F, 59.80%. Found: C, 22.95; Cl, 7.43; F, 59.58%.

Residual nickel salts were contacted with 100 ml of conc. H_2SO_4 and the mixture was extracted with 50 ml then 25 ml of $CF_2ClCFCl_2$. The combined extracts were clarified with $CaSO_4$ and distilled to afford 12.8 g (39% based on nickel carbonyl) of keto alcohol **7**, b.p. 61–62 °C/100 mmHg. IR (CCl_4) (cm^{-1}): 3560 (OH); 1800 (C=O); 1300–1100 (CF, C–O). ^1H NMR ($CDCl_3$) δ: 3.98 (s, OH) ppm. ^{19}F NMR ϕ: −59.3 (A branch d of m, $J_{FF} = 185$ Hz, 1F, CF_2Cl); −60.5 (B branch d of m, $J_{FF} = 185$ Hz, 1F, CF_2Cl); −72.1 (p, $J_{FF} = 10.7$ Hz, 3F, CF_3); −74.9 (t, $J_{FF} = 8.7$ Hz, 3F, $CF_3C{=}O$); −110.8 (A branch d of m, $J_{FF} = 298$ Hz, 1F, CF_2); −111.6 (B branch d of m, $J_{FF} = 298$ Hz, 1F, CF_2) ppm. GC/MS *m/e*: 295 ($M^+ - Cl$); 275 ($M^+ - Cl - HF$); 261 ($M^+ - CF_3$); 233 and 235 ($M^+ - CF_3CO$); 197 ($C_4F_7O^+$); 181 ($CF_2{=}C(CF_3)CF_2^+$); 148 ($CF_3COCF_2H^+$); 147

($CF_3COCF_2^+$); 129 (CF_3COCHF^+); 128 (CF_3COCF^+); 119 ($C_2F_5^+$); 109 ($C_3F_3O^+$); 100 ($C_2F_4^+$); 97 (CF_3CO^+); 85 and 87 (CF_2Cl^+); 78 (CF_2CO^+); 69 (CF_3^+); 51 (CF_2H^+); 50 (CF_2^+). Analysis: Calc. for $C_6HClF_{10}O_2$: C, 21.80; H, 0.30; Cl, 10.73; F, 57.48%. Found: C, 21.86; H, 0.28; Cl, 10.80; F, 57.16%.

Keto alcohol 7 via zinc enolate

A mixture consisting of 6.5 g (0.10 mol) of zinc dust, 100 ml of acetonitrile and 1.0 g of $BrCH_2CH_2Br$ was stirred under N_2 while 36 g (0.20 mol) of chloropentafluoroacetone was distilled in from P_2O_5. After an initial exotherm, stirring was continued at 25 °C for several days, after which volatiles were removed under vacuum and the residue mixed well with 100 ml of conc. H_2SO_4. The product isolated by vacuum transfer was fractionated to afford 21.6 g (65%) of **7**, b.p. 47–49 °C/50 mmHg, as identified by IR spectroscopy.

An attempt to methylate the intermediate Zn salt of **7** with dimethyl sulfate was unsuccessful, indicating low nucleophilicity for the alkoxide.

Polycondensation of 1,3-dichlorotetrafluoroacetone

A mixture consisting of 49.8 g (0.25 mol) of 1,3-dichlorotetrafluoroacetone, 250 ml of dry acetonitrile and 40.6 g (31 ml, 0.24 mol) of nickel carbonyl stirred under a −80 °C condenser rapidly evolved gas and deposited solid within 1 h. After gas evolution had slowed (3 h), stirring was continued overnight. The contents of the −80 °C cold trap (9 ml) were returned to the pot and stirring was continued at 25 °C for a further 6 d. The soft, colorless, insoluble polymer present was essentially involatile, while solvent was removed along with minor amounts of fluorocarbons by warming under vacuum. The residue was extracted with 100 ml then 3×25 ml of 1,1,2-trichlorotrifluoroethane, and the combined extracts filtered and evaporated at 0.1 mmHg to constant weight, giving 22.8 g of a stiff, orange solid. IR (neat) (cm^{-1}): 1800 (C=O); 1690 and 1670 (broad, C=C); 1300–1100 (CF, C–O). Analysis: Calc. for $C_{14}Cl_4F_{19}O_3$: C, 23.39; Cl, 19.73; F, 50.21%. Found: C, 23.20, 23.28; Cl, 19.45, 19.78; F, 49.89, 49.46%.

1,5-Dichloro-1-chlorodifluoromethyl-4-ketohexafluoropentanol-2 (10)

A mixture consisting of 6.5 g (1.0 mol) of zinc dust, 100 ml of acetonitrile and 39.6 g (0.20 mol) of dichlorotetrafluoroacetone was stirred for 3 d and then evaporated to dryness under vacuum. The residual solid was mixed thoroughly with 100 ml of conc. H_2SO_4 and the mixture then extracted twice with $CF_2ClCFCl_2$. The combined organic layers were clarified with $CaSO_4$ and distilled to give 21.1 g (58%) of keto alcohol ***10***, b.p. 60–63 °C/10 mmHg. IR (CCl_4) (cm^{-1}): 3560 (OH); 1770 (C=O); 1200–1100 (CF, C–O). ^{1}H NMR ($CDCl_3$) δ: 4.38 (s, OH) ppm. ^{19}F NMR ϕ: 56.4 (A branch d of m, $J_{FF}=188$ Hz, 2F, CFFCl); −57.8 (B branch d of m, $J_{FF}=188$ Hz, 2F, CFFCl); −65.0 (t, $J_{FF}=11$ Hz, 2F, $ClCF_2C{=}O$); −107.5 (septet, $J_{FF}=11$ Hz, 2F, CF_2) ppm. GC/MS data fit the assigned structure. Analysis: Calc. for $C_6HCl_3F_8O_2$: C, 19.83; H, 0.28; Cl, 29.27; F, 41.82%. Found: C, 19.63; H, 0.43; Cl, 29.45; F, 41.62%.

2-Trifluoromethyl-4-keto-octafluoropentanol-2 (11)

To a stirred mixture consisting of 7.8 g (0.12 mol) of zinc dust, 100 ml of acetonitrile, 3.8 g of dibromoethane, 100 ml of DMF and 33.2 g (0.20 mol) of hexafluoroacetone was added slowly 18.2 g (0.10 mol) of chloropentafluoroacetone. After 4 h, volatiles were removed under reduced pressure and the residue was treated with 100 ml of conc. H_2SO_4. The volatile products, 17.5 g, were distilled to afford 4.2 g (13%) of **11**, b.p. 84–87 °C. IR (CCl_4) (cm^{-1}): 3580 (OH); 1810 (C=O); 1300–1150 (CF, C–O). ^{1}H NMR ($CDCl_3$) δ: 3.93 (s, OH) ppm. ^{19}F NMR ϕ: −73.1 (t, $J_{FF}=11$ Hz, 6F, CF_3); −74.6 (t, $J_{FF}=9$ Hz, 3F, $CF_3C{=}O$); −113.0 (decet, $J_{FF}=10$ Hz, 2F, CF_2) ppm. Analysis: Calc. for $C_6HF_{11}O_2$: C, 22.95; H, 0.32; F, 66.54%. Found: C, 22.75; H, 0.39; F, 66.29%.

*4-Chlorodifluoromethyl-2,2,5,5-tetrafluoro-1,4,6-*tris*(pentafluoroethyl)-3-oxacyclohexanediol-1,6 isomers (13)*

Benzonitrile (100 ml), 28 g (0.12 mol) of 1-chloroheptafluorobutanone-2 and 10.3 g (0.06 mol, 7.8 ml) of $Ni(CO)_4$ were stirred at 25 °C for 1 d. Another 11 g (0.05 mol) of ketone and 10.3 g (0.06 mol, 7.8 ml) of $Ni(CO)_4$ were added and reaction continued for 2 d. Volatiles were removed at 0.1 mmHg and the residue extracted with CH_2Cl_2. Evaporation of the extract gave a soft green solid which was treated with 150 ml of 50% H_2SO_4; three extractions with $CFCl_2CF_2Cl$ gave a solution containing benzonitrile and pinacol **13**. Fractionation afforded 6.8 g (19%) of **13**, b.p. 48–49 °C/0.03 mmHg. IR (neat) (cm^{-1}): 3580, 3500 (OH); 3100 (broad, H-bonded OH); 1250–1100 (CF, C–O) with weak bands for *c*. 5% benzonitrile impurity also present ^{1}H NMR ($CDCl_3$) δ: 5.33 (s, OH) ppm. ^{19}F NMR ϕ: complex spectrum compatible with isomers of **13**. GC/MS (two isomers with very similar spectra) *m/e*: 591 and 593 (M^+-H_2O-F); 575 (M^+-H_2O-Cl); 543 (M^+-CF_2Cl); 525 ($M^+-CF_2Cl-H_2O$); 509 and 511 ($M^+-CF_3CF_2$); 491 and 493 ($M^+-CF_3CF_2-H_2O$) with numerous smaller fragments.

*Dimethyl 1,2-dihydroxy-1,2-*bis*(trifluoromethyl)succinate (14)*

A mixture consisting of 31.2 g (0.20 mol) of methyl trifluoropyruvate, 100 ml of benzonitrile and 17.1 g (0.10 mol, 13 ml) of nickel carbonyl was stirred under nitrogen for 6 d. The volatiles were distilled out at 0.1 mmHg and the residue treated with 100 ml of methanol and 10 ml of conc. H_2SO_4. The resulting solution was evaporated at 50 °C/0.05 mmHg to give a solid residue and some sublimate, which were extracted with 100 ml of ether. Evaporation of the ether, addition of 25 ml of conc. H_2SO_4 to the residue and sublimation at 60–70 °C/0.1 mmHg gave 11.1 g (36%) of pinacol **14** as a mixture of meso and DL pair, m.p. 50–80 °C. An analytical sample, m.p. 60–85 °C, was obtained by recrystallization from 1:1 CH_2Cl_2/pet. ether at −30 °C. IR (Nujol) (cm^{-1}): 3500 and 3430 (OH); 1760 (C=O); 1300–1150 (CF, C−O). ^1H NMR ($CDCl_3$) δ: 4.71 (s, 2H+2H, OH both isomers); 3.99 (s, 6H, OCH_3 one isomer); 3.96 (s, 6H, OCH_3 other isomer) ppm. ^{19}F NMR ϕ: −72.7 (s, 6F, CF_3 one isomer); −73.0 (s, 6F, CF_3 other isomer) ppm; the meso and racemic forms were present in close to 1:1 ratio. GC/MS (first isomer) *m/e*: 315 ($M^+ + H$); 277 ($M^+ - H_2O - F$); 255 ($M^+ - CO_2CH_3$); 245 ($M^+ - CF_3$); 158 ($M/2^+ + H$); 157 ($M/2^+$); 138 ($M/2^+ - F$); 98 (CF_3COH^+); 97 (CF_3CO^+); 79 ($CF_2{=}COH^+$); 78 ($CF_2C{=}O^+$); 69 (CF_3^+); 59 ($CH_3O_2C^+$). The mass spectrum of the second isomer was similar. Analysis: Calc. for $C_8H_8F_6O_6$: C, 30.59; H, 2.57; F, 36.29%. Found: C, 30.60; H, 2.60; F, 35.98%.

Zinc proved to be more efficient as the reductant. To a stirred mixture consisting of 31.2 g (0.20 mol) of methyl trifluoropyruvate and 100 ml of dry DMF was added 13.1 g (0.20 mol) of zinc dust. A rapid exotherm was limited to 50 °C by cooling, the mixture was then stirred overnight, another 2.6 g (0.04 mol) of Zn dust was added, and reaction continued at 25 °C for 1 d. The solvent was removed under reduced pressure and the semisolid residue contacted cautiously with 100 ml of conc. H_2SO_4. The resulting mass was mixed well, then extracted with 100 ml and then 2 × 50 ml of CH_2Cl_2. The extracts were stirred with $CaSO_4$, filtered, evaporated to low volume and the crude solid triturated with 50 ml of petroleum ether to give 19.4 g (62%) of product, m.p. 40–90 °C. Identification as the isomeric mixture **14** was by comparison of the GC/MS spectrum with that of a known sample.

Conclusions

Nickel carbonyl has been shown to be a useful reagent for the preparation of cyclic glycols from α-chlorofluoroketones. The formation of fluorinated keto alcohols from such ketones is better accomplished by the use of zinc. O-benzoylated enols are conveniently obtained from *F*-ketones and nickel carbonyl.

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