107-87-9; 3-phenylpropiophenone, 1083-30-3; *cis*-1,3-diphenylpropene, 1138-83-6; *trans*-1,3-diphenylpropene, 3412-44-0; *cis*-1,3-diphenylprop-2-en-1-ol, 62839-70-7; *cis*-1,3-diphenylprop-2-en-1-one, 614-46-0; *trans*-1,3-diphenylprop-2-en-1-one, 614-47-1; *trans*-pent-3-en-2-one, 3102-33-8.

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The α Effect in α-Chlorofluoro Ketones

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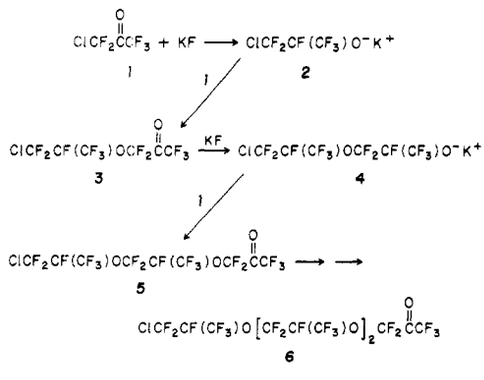
Received July 29, 1977

α-Chloropolyfluoro ketones are subject to displacement of chloride ion under mild conditions by relatively weak bases, notably fluoroalkoxide salts. The latter reagents react with α-chlorofluoro ketones to form fluorinated keto ethers; since these keto ethers add fluoride ion to give new, reactive fluoroalkoxides, a series of low oligomers is produced in each case. The new fluorinated keto ethers are shown to resemble hexafluoroacetone in their response to free radicals as well as to fluoride ion.

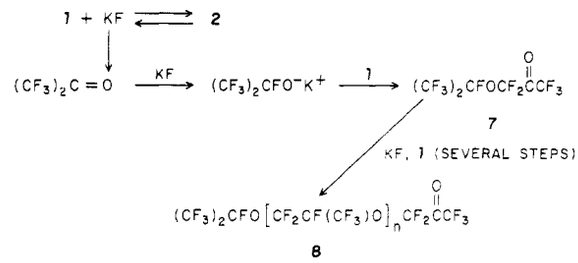
Anionic attack on saturated carbon with displacement of a substituent X^- is rarely encountered in highly fluorinated systems. If reaction with the fluorinated substrate does occur, the incoming base most frequently attacks a nonfluorine substituent with displacement of fluorocarbanion.[1] The known cases of intermolecular nucleophilic attack at sp^3 carbon in fluorinated compounds seem to be limited to those in which a carbonyl group is α to the leaving group X, and the nucleophile has usually been fluoride ion.[2] The results described below further define the conditions under which such reactions occur and demonstrate a wider scope for the reaction by the use of some other types of nucleophile.

Fluoroalkoxides. Chloropentafluoroacetone (1) in dimethylformamide reacts easily with 1 equiv of potassium fluoride to give the soluble adduct **2** which only slowly undergoes further change at 25 °C. In the presence of excess **1**, however, displacement of chloride ion by chlorohexafluoroisopropoxide ion **2** occurs to form the new ketone **3** (Scheme I). The reaction proceeds slowly at 25 °C and more rapidly at

Scheme I



Scheme II



temperatures up to 80 °C. Moreover, ketone **3** has a relatively unhindered carbonyl group and competes successfully with **1** for fluoride ion to form the fairly stable adduct fluoroalkoxide **4.** The latter also displaces chloride ion from **1** to form the higher fluoro ketone **5.** Ketone **5** and its higher analogues similarly form reactive alkoxides by addition of fluoride ion with the net result that a series of fluorinated keto polyethers is formed in diminishing yield as molecular weight increases. After the first displacement, each subsequent displacement will be seen to have the effect of introducing a unit of hexafluoropropene epoxide.[3]

Yields obtained with a 1:2 KF/**1** mol ratio in dimethylformamide have been 30% for **3** and 14% for **5** with about 12% conversion to by-product hexafluoroacetone. In addition, a related series of by-products is formed in amounts that increase with increase in proportion of KF. These by-products contain no chlorine and result from formation of hexafluoroacetone and its subsequent reaction as indicated in Scheme II. Coreaction of both **1** and hexafluoroacetone with KF gave preparative yields of these by-products, and ketones **7** and **8** ($n = 1, 2$) were isolated.[4]

A reaction of **1** with KF carried out in triglyme proceeded very slowly at 40–80 °C, so the temperature was raised to 95

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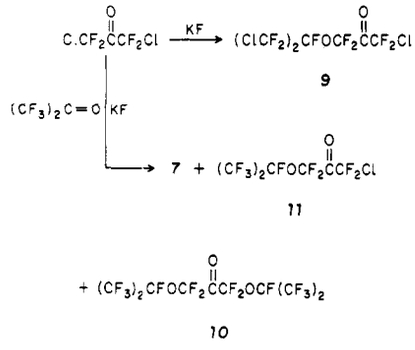
Scheme III

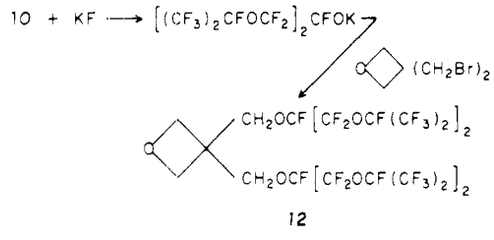


°C; reflux from a −80 °C condenser slowly lowered the temperature to 80 °C. Distillation gave a low yield of the cleavage product, trifluoroacetyl fluoride, and 39% of hexafluoroacetone along with 8% of **3** and 5% of **5**. Presumably, the higher temperatures led predominantly to displacement by fluoride ion because the fluoroalkoxides such as **2** were largely dissociated.[5]

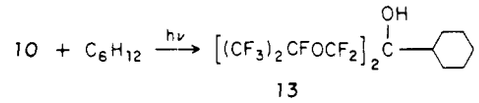
sym-Dichlorotetrafluoroacetone reacted with KF at 50 °C to give a low conversion to ketone **9**. Incorporation of hexafluoroacetone into the reaction mixture resulted in a preparative route to perfluoro ketone **10** along with monochloro ketone **11** (Scheme III) as well as ketone **7**.

As a test of the reversibility of the reaction by which **10** was formed, a mixture of KF and **10** in dimethylformamide was stirred at 25 °C until it became homogeneous and then was heated at 80–85 °C. No volatiles were detected, and **10** was recovered in 91% yield. Under conditions of synthesis, therefore, keto ethers such as **10** appear to be stable toward displacement of heptafluoroisopropoxide.

The fluorinated keto α-ethers resemble hexafluoroacetone in response to base in that substitution apparently does not occur and steric hindrance to attack at the electrophilic carbonyl carbon is low. The fluoroalkoxide from fluoride ion and **10** has good stability with respect to dissociation and is fairly nucleophilic, as was shown by its reaction with 3,3-bis(bromomethyl)oxetane to form oxetane **12** in 70% yield. Similar results have been obtained with hexafluoroacetone.[6]

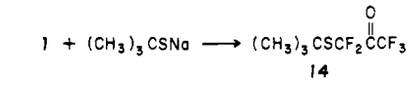


The reactivity of **10** toward alkyl radicals is also similar to that of hexafluoroacetone,[7] as exemplified by the radical chain reaction of **10** with cyclohexane to form carbinol **13** in 74% yield.

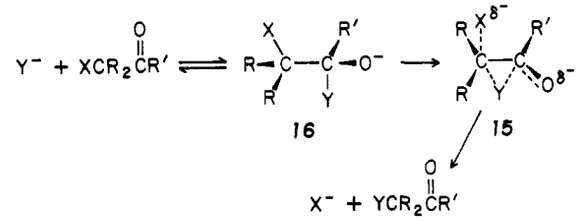


Discussion

The possibility that weak bases which add reversibly to the carbonyl carbon are required to successfully displace chloride from an α-chloropolyfluoro ketone was tested in a reaction with mercaptide. Chloropentafluoroacetone (**1**) reacted readily with sodium *tert*-butylmercaptide to give sulfide **14**. In contrast, sodium methoxide, which gives a stable adduct with **1** at −15 °C, led to a spectrum of decomposition products at 40 °C. These results support the idea that only weak bases and not strong ones give the reaction.



Although S_N2 attack at sp^3 carbon in highly fluorinated systems is unusual and perhaps unprecedented under such mild conditions, we appear to have here a special case of the well-recognized α effect in which a carbonyl group enhances the rate of replacement of an α substituent.[8] A commonly accepted picture involves triangular transition state **15**. The shielding effect by fluorine atoms on saturated carbon which resists direct penetration by a nucleophile could be mitigated in the presence of an adjacent carbonyl group, since the nucleophile could reversibly form adduct **16**, from which **15** would be readily accessible in the absence of side reactions such as haloform cleavage.



For the fluoro ketone case (in which R is F and R′ is fluoroalkyl) delocalization of negative charge onto oxygen in the transition state may reduce the noramlly high energy associated with unfavorable interactions with fluorine on sp^2 carbon. In a transition state resembling **15**, the bond to fluorine could even be more nearly sp^3 than sp^2. Thus, reversible addition of nucleophile to the carbonyl carbon apparently results in an appreciable fraction of occurrences in **15**, a pathway not available to completely saturated fluoroalkyl chlorides.

Loosening of the bond to leaving group X seems to be essential to a readily accessible transition state. Chloride ion is a sufficiently good leaving group, but fluoride and fluoroalkoxide are too strongly bonded to carbon to be readily displaced.

Another mechanistic possiblity after addition of nucleophile Y^- to the carbonyl group is bridging by carbonyl oxygen to form epoxide. Since such an epoxide intermediate would be expected to form readily after addition of fluoride ion, but does not, and since direction of subsequent ring opening would have to be highly specific to give ketone rather than acid fluoride, this mechanism is considered unlikely.

An attempted extension of the displacement of α-chlorines to an α-chloro ester,[9] methyl chlorodifluoroacetate, resulted in ready methylation of the anion in preference to either displacement of chloride or haloform cleavage.

Experimental Section

Infrared spectra were recorded on a Perkin Elmer 21 spectrophotometer with 20% solutions in CCl_4 unless otherwise specified. ^1H NMR spectra were taken on a Varian A-60 spectrometer in carbon tetrachloride with tetramethylsilane as internal standard; ^{19}F NMR spectra were taken on a Varian XL-100 spectrometer with the downfield direction from $CFCl_3$ as internal standard taken as positive. GLC purifications were carried out on 25% Fluorosilicone 1265 on Chromosorb W with a He flow rate of 400 mL/min.

Perfluoro-5-chloromethyl-4-oxahexanone-2 (3), Perfluoro-8-chloromethyl-5-methyl-4,7-dioxanonanone-2 (5), and Perfluoro-11-chloromethyl-5,8-dimethyl-4,7,10-trioxadodecanone-2 (6). A suspension of 10.5 g (0.18 mol) of anhydrous KF in 150 mL of dry dimethylformamide was stirred while 65.6 g (0.36 mol) of chloropentafluoroacetone was distilled in. The homogeneous reaction mixture was stirred at 50 °C for 2 h and then at 70 °C for 1 h, during

which time KCl precipated. A stillhead was attached, and the pot contents were raised slowly to 155 °C while 38.2 g of distillate was taken, bp 25–140 °C. Appreciably more KCl formed during this operation. Fractionation of volatiles collected in the cold trap and identification of the gases by IR showed 20% of chloropentafluoroacetone was recovered and 13% was converted to hexafluoroacetone. Fractionation of the liquid distillate from concentrated H_2SO_4 afforded 14.9 g (24% conversion) of **3**, bp 80–83 °C, and 6.8 g (11% conversion) of **5**, bp 64 °C (50 mmHg). Higher boiling oligomers were also present.

A similar reaction carried out at 25 °C for 6 days and 50 °C for 1 day, then worked up the same way, gave similar yields and conversions.

A ratio of $KF/ClCF_2COCF_3$ significantly greater than 0.5 led to an increased yield of oligomers derived from heptafluoroisopropoxide anion at the expense of chlorodifluoromethyl-terminated oligomers. An apparent increase in the relative amount of higher oligomers was also observed. Reaction of 16.8 g (0.29 mol) of KF and 65.6 g (0.36 mol) of chloropentafluoroacetone was carried out in 150 mL of dry dimethylformamide. After 3 days at 25 °C, only a minor amount of solid was deposited, in contrast to the reaction above. After 4 days at 40 °C, more KCl precipitated, and, after 2 days at 70 °C, considerable salt had precipitated. Distillation of the products followed by redistillation of the liquid products from H_2SO_4 gave ca. 1% of recovered $ClCF_2COCF_3$, 17% yield of hexafluoroacetone, 18% yield or 11.1 g of **3**, and 11% yield or 7.0 g of **5**. Intercut sizes and the presence of impurities detectable by GC indicated that hexafluoroacetone produced in the reaction had initiated the formation of a series of perfluorinated oligomers. This supposition was supported by the isolation of **7**, bp 55–56 °C, 2.7 g (5%) (see below for characterization). A higher boiling fraction, 4.5 g, bp 96–100 °C (50 mm), gave 2.3 g (4%) of **6** by GLC.

For **3**: IR (CCl_4) 5.54 μm (C=O); mass spectrum *m/e* 185 ($CF_3C^+FCF_2Cl$ with ^{37}Cl at 187), 147 ($CF_3COCF_2^+$), 97 (CF_3CO^+), 85 (CF_2Cl^+ with ^{37}Cl at 87), and 69 (CF_3^+); NMR (^{19}F) −68.8 (m, 2 F, CF_2Cl), −75.1 (t, J_{FF} = 4.5 Hz, atop broad m, 5 F, $CF_3CO + OCF_2$), −79.0 (m, 3 F, CF_3CF), and −140.3 ppm (t, J_{FF} = 21.5 Hz, of m, 1 F, CF). Anal. Calcd for $C_6ClF_{11}O_2$: C, 20.68; Cl, 10.17. Found: C, 20.57; Cl, 10.15.

For **5**: IR (CCl_4) 5.53 μm (C=O); mass spectrum *m/e* 313 ($M^+ - CF_3CFO(CF_2Cl)$), 185 ($CF_3CF^+CF_2Cl$ with ^{37}Cl at 187), 169 ($C_3F_7^+$), 147 ($CF_3COCF_2^+$), 97 (CF_3CO^+), 85 (CF_2Cl^+ with ^{37}Cl at 87), and 69 (CF_3^+); NMR (^{19}F) −69.0 (m, 2 F, CF_2Cl), −75.3 (rough t, J_{FF} = 4 Hz, atop broad m, 5 F, $CF_3CO + OCF_2$), −79.2 (m, 3 F, CF_3CCF_2Cl), −80.6 (m, 5 F, CF_3CFCF_2O), −141.1 (t, J_{FF} = 19 Hz, of m, 1 F, $CFCF_2Cl$), and −145.0 ppm (t, J_{FF} = 20 Hz of m, 1 F, $CFCF_2O$). Anal. Calcd for $C_9ClF_{17}O_3$: C, 21.01; Cl, 6.89. Found: C, 21.08; Cl, 6.31.

For **6**: IR (CCl_4) 5.54 μm (C=O); NMR (^{19}F) −69.0 (broad, 2 F, CF_2Cl), −75.3 (t, J_{FF} = 5 Hz, atop broad m, 5 F, CF_3COCF_2), −79.2 (m, 3 F, CF_3CCF_2Cl), −80.6 (m, 10 F, $2CF_3CFCF_2O$), −141.0 (broad, 1 F, $CFCF_2Cl$), 144.8 (broad, 1 F, $CFCF_2O$), and −145.4 ppm (broad, 1 F, $CFCF_2O$). Anal. Calcd for $C_{12}ClF_{23}O_4$: C, 21.18; Cl, 5.21. Found: C, 20.81; Cl, 5.23.

Perfluoro-5-methyl-4-oxahexanone-2 (7), Perfluoro-5,8-dimethyl-4,7-dioxanonanone-2 (8, *n* = 1), and Perfluoro-5,8,11-trimethyl-4,7,10-trioxadodecanone-2 (8, *n* = 2). Increased amounts of perfluoro ketone ethers can be obtained by replacing part of the chloropentafluoroacetone with hexafluoroacetone. With only equimolar amounts of hexafluoroacetone and KF present, sufficient products **7** and **8** (*n* = 1, 2) were formed for them to be isolated. A mixture of 10.5 g (0.18 mol) of KF, 150 mL of dry dimethylformamide, 29.9 g (0.18 mol) of hexafluoroacetone, and 33.7 g (0.18 mol) of chloropentafluoroacetone was stirred and refluxed at 35–40 °C for 2 days, then 45–50 °C for 3 days, and at 55 °C for 2 days. Distillation gave 43.2 g, bp 60–150 °C, along with 56% of recovered hexafluoroacetone. Fractionation of the liquid products by distillation gave 14.3 g (24% based on chloro ketone 1), bp 56–59.5 °C: GC showed the product boiling near 59 °C to be pure **7**; IR (CCl_4) 5.54 μm (C=O); mass spectrum *m/e* 313 ($M^+ - F$), 263 ($M^+ - CF_3$), 235 ($(CF_3)_2CFOCF_2$), 169 ($C_3F_7^+$), 147 ($CF_3COCF_2^+$), 97 (CF_3CO^+), 69 (CF_3^+); mass calcd for $C_6F_{11}O_2$, 312.9722; found, 312.9763; NMR (^{19}F) −75.2 (t, J_{FF} = 5.6 Hz, 3 F, CF_3CO), −75.8 (d, J_{FF} = 21.2 Hz, of q, J_{FF} = 5.6 Hz, of septets, J_{FF} = 5.5 Hz, 2 F, OCF_2), −81.4 (t, J_{FF} = 5.5 Hz, of d, J_{FF} = 2.3 Hz, 6 F, CF_3), and −145.4 ppm (t, J_{FF} = 21.2 Hz, of septets, J_{FF} = 2.3 Hz, 1 F, CF). Anal. Calcd for $C_6F_{12}O_2$: C, 21.70; F, 68.66. Found: C, 21.42; F, 68.85.

Fractions with bp 115–117 °C were 6.0 g (13% based on **1**) of crude **8** (*n* = 1). An analytical sample was obtained by GLC: IR (CCl_4) 5.52 μm (C=O); NMR (^{19}F) −75.3 (t, J_{FF} = 5 Hz, atop m, 5 F, CF_3COCF_2), −80.7 (m, 3 F, CF_3CFCF_2), −81.2 (broad, 2 F, OCF_2CF), −81.5 (m, 6 F, $(CF_3)_2CF$)), −145.0 (t, J_{FF} = 21 Hz, 1 F, $(CF_3)_2CF$), and −146.0 ppm (t, J_{FF} = 20 Hz, 1 F, CF_3CFCF_2). Anal. Calcd for $C_9F_{18}O_3$: C, 21.70; F, 68.66. Found: C, 21.30; F, 68.38.

A fraction with bp 92–93 °C (50 mmHg) was 1.5 g (based on **1**) of crude **8** (*n* = 2). An analytical sample was obtained by GLC: IR (CCl_4) 5.54 μm (C=O); NMR (^{19}F) −75.6 (t, J_{FF} = 5.5 Hz, atop broad m, 5 F, CF_3COCF_2), −80.7 (m, 6 F, 2 CF_3CFCF_2), −81.2, (broad, 4 F, 2 OCF_2CF), −81.5 (m, 6 F, $(CF_3)_2CF$), −144.9 (broad m, 1 F, $(CF_3)_2CF$), and −145.8 ppm (broad m, 2 F, CF_3CFCF_2).

Perfluoro-1,6-dichloro-5-chloromethyl-4-oxahexanone-2 (9). A mixture of 10.5 g (0.18 mol) of KF and 150 mL of dry dimethylformamide was stirred at 15 °C while 71.6 g (0.36 mol) of dichlorotetrafluoroacetone was added rapidly. After 1 day at 45–50 °C, the mixture was distilled to give 64% of crude recovered ketone and 10.8 g of a liquid which was redistilled from H_2SO_4. There was thus obtained 3.1 g (5% conversion and 13% yield) of **9**: bp 73–75 °C (80 mmHg); IR (CCl_4) 5.53 μm (C=O); NMR (^{19}F) −65.9 (m, 6 F, CF_2Cl), −72.2 (d, J_{FF} = 21.3 Hz, of t, J_{FF} ~ 6.5 Hz, of overlapping pentets, J_{FF} ~ 6.5 Hz, 2 F, OCF_2), and −135.4 ppm (t, J_{FF} = 21.3 Hz, of overlapping pentets, J_{FF} = 5.4 Hz, 1 F, CF). Anal. Calcd for $C_6Cl_3F_9O_2$: C, 18.89; Cl, 27.89. Found: C, 18.84; Cl, 27.66.

Perfluoro-1-chloro-5-methyl-4-oxahexanone-2 (11) and Perfluoro-2,8-dimethyl-3,7-dioxanonanone-5 (10). A mixture of 21.0 g (0.36 mol) of dry KF, 150 mL of dry dimethylformamide, 59.8 g (0.36 mol) of hexafluoroacetone, and 35.8 g (0.18 mol) of dichlorotetrafluoroacetone was heated at reflux (40–60 °C) for 3 days. Distillation afforded 63 g of liquid, bp 30–145 °C, along with 16.5 mL at −80 °C (46%) of recovered hexafluoroacetone. Redistillation from H_2SO_4 gave 18.7 g (21% conversion and 39% yield from hexafluoroacetone) of **10**, bp 117–118 °C. A center-cut, single component by GC, was analyzed: IR (CCl_4) 5.51 μm (C=O); mass spectrum *m/e* 479 ($M^+ - F$), 313 ($M^+ - F - HFA$), 263 ($M^+ - F - HFA - CF_2$), 235 ($(CF_3)_2CFOCF_2^+$), 169 ($C_3F_7^+$), 147 ($CF_3COCF_2^+$), 97 (CF_3CO^+); NMR (^{19}F) −75.0 (d, J_{FF} = 21.5 Hz, of septets, J_{FF} = 5.5 Hz, 2 F, OCF_2), −81.4 (m, 6 F, CF_3), and −145.3 ppm (t, J_{FF} = 21.5 Hz, of septets, J_{FF} = 2.1 Hz, 1 F, CF). Anal. Calcd for $C_9F_{18}O_3$: C, 21.70; F, 68.66. Found: C, 21.60; F, 68.59.

Many coproducts form along with **10**, including the expected intermediate **11** and its fluoride ion displacement product **7**. These compounds were obtained from a larger scale reaction along with substantial amounts of mixed high-boiling products. A reaction of 87.1 g (1.5 mol) of KF, 500 mL of dimethylformamide, 250 g (1.5 mol) of hexafluoroacetone, and 149.5 g (0.75 mol) of dichlorotetrafluoroacetone was stirred and heated at 45–60 °C for 1 week. Distillation gave 78 mL at −80 °C (52% recovery) of crude hexafluoroacetone and 244 g of liquid, bp 45–140 °C. Distillation from H_2SO_4 gave 20.5 g (8% conversion based on dichloro ketone) of **7**, bp 58–60 °C, identified by ^{19}F NMR; 17.5 g (7% yield based on dichloro ketone) of **11**, bp 84–86 °C; 81.5 g (22% conversion and 45% yield from hexafluoroacetone) of **10**; and 68.2 g of mixed fluorinated higher boilers. A sample of **11**, one component by GC, was analyzed: IR (neat) 5.54 μm (C=O); NMR (^{19}F) −66.2 (t, J_{FF} = 7.5 Hz, 2 F, CF_2Cl), −73.5 (d, J_{FF} = 21.5 Hz, of m, 2 F, OCF_2), −81.3 (t, J_{FF} = 5.7 Hz, of d, J_{FF} = 1.2 Hz, 6 F, CF_3), and −145.6 ppm (t, J_{FF} = 21.5 Hz, of septets, J_{FF} = 1.2 Hz, 1 F, CF). Anal. Calcd for $C_6ClF_{11}O_2$: C, 20.68; Cl, 10.17; F, 59.97. Found: C, 20.90; Cl, 10.01; F, 59.68.

Cyclohexylbis(perfluoroisopropoxymethyl)carbinol (13). A solution of 20.0 g (0.04 mol) of **10** and 33.6 g (0.40 mol) of cyclohexane in 50 mL of trichlorotrifluoroethane was stirred and irradiated under nitrogen with a low-pressure helical mercury lamp placed around the quartz reaction tube. Irradiation was continued for 5 h with the temperature at 40–50 °C. Distillation gave 17.3 g (74%) of adduct **13**: bp 99–100 °C (10 mmHg); $n^{24}D$ 1.3388; IR (neat) 2.74 (OH), 3.37 and 3.46 (satd CH), 8–9 μm (CF, C–O); NMR (^1H) 2.82 (s, 1 H, OH) and 1–2.3 ppm (m, 11 H, CH); NMR (^{19}F) −73.2 (m, 2 F, OCF_2), −80.8 (m, 6 F, CF_3), and −145.6 ppm (t, J_{FF} = 23 Hz, of septets, J_{FF} = 2 Hz, 1 F, CF). Anal. Calcd for $C_{15}H_{12}F_{18}O_3$: C, 30.94; H, 2.08; F, 58.73. Found: C, 31.10; H, 2.13; F, 58.62.

***tert*-Butylthiopentafluoroacetone (14).** A suspension of 9.6 g (0.2 mol) of 50% NaH/mineral oil in 150 mL of dry dimethylformamide was stirred at 10–15 °C while 23.4 g (0.26 mol) of *tert*-butylmercaptan was added dropwise. When H_2 evolution was complete, 36.5 g (0.20 mol) of chloropentafluoroacetone was distilled into the cooled mixture. The mixture was then stirred and warmed from 15 to 40 °C, where solid precipitated and a mild exotherm occurred. The mixture was heated at 55–60 °C for 2.5 h and then distilled to give 35 g of crude products, bp 50–85 °C (100 mmHg). Redistillation afforded 12.6 g (27%) of **14**, bp 61–68 °C (100 mmHg), purified further by GLC for analysis: IR (neat) 3.33, 3.42, and 3.46 (saturated CH), 5.59 (C=O), 7.14 and 7.28 ($(CH_3)_3C$), and 8–9 μm (CF); NMR (^1H) 1.56 ppm (s, CH_3); NMR (^{19}F) 73.6 (t, J_{FF} = 7.9 Hz, 3 F, CF_3), −83.4 ppm (q, J_{FF}

= 7.9 Hz, 2 F, CF_2). Anal. Calcd for $C_7H_9F_5OS$: C, 35.60; H, 3.84; S, 13.57. Found: C, 35.33; H, 3.76; S, 13.38.

3,3-Di[bis(perfluoroisopropoxymethyl)fluoromethoxymethyl]oxetane (12). A mixture of 3.9 g (0.067 mol) of KF, 33.4 g (0.067 mol) of ketone **10**, 7.8 g (0.032 mol) of 3,3-bis(bromomethyl)oxetane, and 75 mL of dry dimethylformamide was stirred until homogeneous and then heated at 65–70 °C for 2 days and at 80 °C for 6 h. Dilution with 500 mL of water gave a lower layer which was washed with water, dried, and distilled to afford 24.9 g (70%) of oxetane **12**: bp 85 °C (0.05 mmHg); IR 3.35 and 3.45 (saturated CH), 7.5–9 (CF, C–O), and 10.10 μm (oxetane ring); NMR (^{1}H) 4.37 (s, 1, oxetane CH_2) and 4.30 (broad s, 1, CH_2OCF); NMR (^{19}F) −78.8 (broad m, 4, CF_2O), −81.4 (m, 12, CF_3), −142.6 (m, 1, CH_2OCF), and −146.0 ppm (t of m, J_{FF} = 21.8 Hz, 2, CF_2OCF). Anal. Calcd for $C_{23}H_8F_{38}O_7$: C, 24.71; H, 0.72; F, 64.56. Found: C, 24.74; H, 0.85; F, 64.35.

Registry No.—**1**, 79-53-8; **3**, 64457-48-3; **5**, 64457-49-4; **6**, 64457-50-7; **7**, 64457-51-8; **8** (n = 1), 64457-52-9; **8** (n = 2), 64457-53-0; **9**, 64457-54-1; **10**, 64457-55-2; **11**, 64457-56-3; **12**, 64457-57-4; **13**, 64457-58-5; **14**, 64457-59-6; hexafluoroacetone, 684-16-2; 1,3-dichlorotetrafluoroacetone, 127-21-9; cyclohexane, 110-82-7; *tert*-butylmercaptan, 75-66-1; 3,3-bis(bromomethyl)oxetane, 2402-83-7.

References and Notes

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Hydroformylation Catalyzed by Cis-Chelated Rhodium Complexes. Extension to Polymer-Anchored Cis-Chelated Rhodium Catalysts

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Received July 29, 1977

The chelating phosphine ligands $Ph_2PCH_2CH_2PPh_2$, $Ph_2PCH_2CH_2CH_2PPh_2$, and $Ph_2P(CH_2)_4PPh_2$ have been examined as ligands in the rhodium catalyzed hydroformylation of 1-pentene and 2-pentene. 1,2-Bis(diphenylphosphino)ethane causes a large decrease in the normal/branched (n/b) selectivity of 1-pentene hydroformylations at 60–120 °C and 100–800 psi. Increasing addition of PPh_3 causes increased n/b ratios. Hydroformylations of 2-pentene with $Ph_2PCH_2CH_2PPh_2$ exhibited low n/b selectivities which increased as pressure was lowered and temperature was raised. Using a polymer-anchored version of the catalyst (i.e., Ⓟ-$C_6H_4P(Ph)CH_2CH_2P(Ph_2)RhH(CO)L$) selectivities of 40–42% hexanal could be obtained from 2-pentene at 140 °C and 100–400 psi. The inherent propensity toward anti-Markownikoff rhodium hydride addition to a terminal double bond is lower for *cis*-phosphine chelated rhodium hydrides than for *trans*-bisphosphine–rhodium hydride complexes. This is attributed to differences in steric effects.

Phosphines and arsines have long been investigated as ligands for rhodium in the hydroformylation of olefins.[1] Detailed mechanistic investigations of hydroformylation were reported by Wilkinson et al.[2-4] using $RhH(CO)(PPh_3)_3$ as the catalyst. It has been found that rhodium complexes are more active "oxo" catalysts than cobalt compounds, permitting their use at low temperatures to give a minimum of by-products.[5] In general, rhodium-catalyzed hydroformylations are performed at temperatures from 40 to 140 °C and pressures from 50 to 1500 psi.[6] Under these conditions the selectivity to aldehydes is often greater than 99%.

Addition of tertiary phosphine ligands to rhodium-catalyzed hydroformylations greatly reduces the tendency for double bond isomerization. For example, 1-pentene was converted to 72% *n*-hexanal and 28% 2-methylpentanal in the presence of $RhH(CO)(PPh_3)_3$.[7] Similar selectivities were reported by Osborn, Wilkinson, and Yang[2] using $Rh(CO)Cl(PPh_3)_2$ and by Pruett and Smith[8] using a triphenyl phosphite–rhodium complex. Roth et al.[7] demonstrated that increasing additions of triphenylphosphine to $Rh(CO)Cl(PPh_3)_2$ resulted in a higher selectivity to *n*-heptanal from 1-hexene, while Pruett and Smith[8] observed a similar effect upon addition of excess triphenyl phosphite to $RhH(CO)(P(OPh)_3)_3$. High rates and very high terminal selectivities were observed by Brown and Wilkinson[9] when $RhH(CO)(PPh_3)_3$ was used in molten triphenylphosphine at 85–150 °C.

Recently, increased attention has been given to attaching homogeneous catalysts to polymer supports.[10-14] It is now well established that polymer-anchored $RhH(CO)(PPh_3)_3$ exhibits considerably higher selectivities than its homogeneous analogue, when the resin to which it is anchored has high P/Rh ratios and high loadings of phosphine.[12,14] At 1:1 H_2/CO, normal to branched (n/b) selectivities as high as 20:1 have been observed,[15] and by varying the H_2:CO ratios n/b selectivities up to 64:1 were achieved.[14]

Despite the extensive selectivity studies already reported, very little work describes the effect that cis-chelating phosphines exert in hydroformylation reactions. The n/b selectivity using $RhH(CO)(PPh_3)_3$ is strongly dependent on the position of equilibrium between $RhH(CO)_2(PPh_3)_2$ and $RhH(CO)_2PPh_3$.[2-4,16] This is summarized in Scheme I. The associative pathway, which leads to higher n/b selectivities,[2-4,16] proceeds mainly by anti-Markownikoff rhodium hydride addition of $RhH(CO)_2(PPh_3)_2$ to the terminal carbon. When two phosphine ligands are bound to rhodium, selectivity is higher. This suggested that a chelating ligand, such as bis(diphenylphosphino)ethane (see complex **1**, Scheme II), might give high n/b selectivities because this ligand would keep two

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