# CONCLUSIONS

Water molecules in partially dehydrated zeolite directly interact with  $Na^+$  cations. The final three or four water molecules per unit cell removed upon the dehydration of zeolite are apparently bound to  $Na^+$  cations of the eight-membered windows, while the previous ~10 molecules are bound to  $Na^+$  cations of six-membered windows.

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# REACTION OF METHYLMAGNESIUM IODIDE WITH PERFLUOROCARBOXYLATE ESTERS

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Methyl perfluoroalkyl ketones are used in the synthesis of nitriles of perfluoroalkylsubstituted acrylic acids and other compounds used for the preparation of fluorine-containing polymers. Chen et al. [1, 2] have developed a general method for the preparation of such ketones by the reaction of perfluorocarboxylate esters with several organolithium compounds

$$\begin{array}{c} \overset{O}{\operatorname{R}_{F}-C-OR} + R'Li \xrightarrow{-78^{2}} \left[ \begin{array}{c} \overset{O}{\operatorname{Ch}} \\ R_{F}-C-OR \\ R' \end{array} \right] \xrightarrow{1. < -30^{\circ}} R_{F}-C-R' \\ \overset{O}{\operatorname{Ch}} \\ \overset{(I)}{\underset{1. > -30^{\circ}}{}} \\ \overset{O}{\operatorname{Ch}} \\ \overset{I}{\underset{2. H^{+}(H_{2}O)}{}} R_{F}-\overset{I}{\underset{R'}{}} \\ \overset{R}{\operatorname{Ch}} \\ \end{array} \right]$$

where  $R_{\mathbf{F}} = CF_3$ ,  $C_2F_5$ ,  $C_2F_5(OC_2F_4)_n OCF_2$ ;  $R' = C_6H_5$ ,  $C_6F_5$ ,  $BrC_6H_4$ ,  $C_3H_7$ ;  $R = CH_3$ ,  $C_2H_5$ .

When  $R_F = C_3 F_7 (OCFCF_2)_n OCF$  and  $i-C_3 H_7$ , the formation and decomposition of the intermediate oc-

cur at -110°C with the formation of olefins. The formation of a tertiary alcohol was attributed by these authors to the decomposition of (I) above -30°C and the reaction of the ketone formed with a new molecule of organolithium compound.

On the other hand, the question of the effect of the nature of the alkyl group in the ester on the tertiary alcohol/ketone product ratio in the presence of organometallic compounds has not been studied sufficiently. Understanding this effect is important for improving the selectivity of ketone formation. We studied the dependence of the yields of the ketone and alcohol products both on the temperature and alkyl group structure for the reaction between MeMgI and perfluoroenanthic and perfluoroadipic acids (Tables 1 and 2).

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R in <b>es</b> ter	т, С	Time, h	Yield, %		Conversion
			ketone	alcohol	- %
CH <sub>3</sub> C <sub>2</sub> H <sub>5</sub> C <sub>2</sub> H <sub>5</sub> CH (CH <sub>3</sub> ) <sub>2</sub> CH (CH <sub>3</sub> ) <sub>2</sub>	$ \begin{array}{ c c } -70 \\ -45 \\ -30 \\ -40 \\ -20 \\ \end{array} $	6 5 2 5 2	64 * · 76 71 77 73 *	6 * 0 * 5 * 0 * 4 *	91 * 100 * 100 * 100 * 100 *

TABLE 1. Reaction of Methylmagnesium Iodide with Perfluoroenanthate Esters

\*Determined by gas-liquid chromatography and NMR spectroscopy.

TABLE 2. Reaction of Methylmagnesium Iodide with Adipic Acid Esters

R in ester	T, °C	Diketone yield, %
CH <sub>3</sub>	-78	24 *
C <sub>2</sub> H <sub>5</sub>	-58	53 *
C <sub>2</sub> H <sub>5</sub>	-45	78
C <sub>2</sub> H <sub>5</sub>	-35	71 *
CH (CH <sub>3</sub> ) <sub>2</sub>	-35	55 *

\*Determined by gas-liquid chromatography and NMR spectroscopy.

The experimental results indicate that the stability of the hemiketal salt increases with increasing bulk of the alkyl radical. Chen et al. [1] have indicated the reverse order for the stability of lithium salts. However, in our case, the thermal stability of such salts was not studied for the pure compounds and MeMgI was present in the reaction mass. The formation of the tertiary alcohol may be explained either by catalysis of the decomposition of the hemiketal salt to the ketone by means of the organomagnesium compound or by the direct substitution in the salt at the quaternary carbon atom [3].

The reaction of MeMgI and diesters of perfluoroadipic acid has its own special features



 $R = CH_3, C_2H_5, CH(CH_3)_2.$ 

The addition of a second MeMgI molecule proceeds significantly more slowly than the addition of the first due either to the low solubility of (II) below  $-35^{\circ}$ C or intramolecular ring formation [4]. About 40% ketoester (IV), 4% hydroxyester (V), and 4% ketoalcohol (VII) are formed in addition to the diketone when the dimethyl ester of difluoroadipic acid was used.

The conversion of (II) to (III) proceeds extremely slowly in the case of the diisopropyl ester even at -35°C, which accounts for the low diketone yield.

The best results are obtained using the diethyl ester of perfluoroadipic acid. In this case, products other than the diketone were not formed.

## EXPERIMENTAL

The <sup>19</sup>F and <sup>1</sup>H NMR spectra were taken on a WM-250 spectrometer at 236 and 250 MHz, respectively, as 1% solutions in CDCl<sub>3</sub> relative to CFCl<sub>3</sub> and HMDS, respectively. The IR spectra were taken on a UR-20 spectrometer. Gas-liquid chromatography was carried out on an LKhM-8MD chromatograph using 3 mm × 3m columns packed with 10% SKTFT on Chromosorb W. Ether was distilled over  $P_2O_5$  and stored over sodium wire.

<u>Methyl Perfluorohexyl Ketone</u>. MeMgI was obtained from 26.4 g (1.1 moles) Mg and 158 g (1.1 moles) MeI in 300 ml abs. ether. An additional 700 ml ether was added and the solution was cooled in a nitrogen stream to  $-78^{\circ}$ C. A solution of 0.51 mole perfluoroenanthate ester in 300 ml ether cooled to  $-78^{\circ}$ C was then added with efficient stirring over 3 min. The reaction mass was stirred at the temperatures and over the times indicated in Table 1 and decomposed with 80 ml concentrated hydrochloric acid in 70 ml ethanol such that the temperature did not rise over the reaction temperature. Then, 250 ml water was added and the mixture was brought to 20°C. The ethereal layer was separated and washed with 100 ml sat. aq. K<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>SO<sub>3</sub>. The aqueous layers were combined and extracted with two 100-ml portions of ether and the combined extracts were dried over MgSO<sub>4</sub>. Distillation gave methyl perfluorohexyl ketone, bp 128-129.5°C (748 mm). PMR spectrum ( $\delta$ , ppm, J, Hz): 2.35 (CH<sub>3</sub>), J<sub>H-\alpha-CF<sub>2</sub> = 1.9, J<sub>H-\beta-CF<sub>2</sub> = 0.8. <sup>19</sup>F NMR spectrum ( $\delta$ , ppm): 122.2 (2F,  $\alpha$ -CF<sub>2</sub>), 123.5 (2F,  $\beta$ -CF<sub>2</sub>), 124.2 (2F,  $\gamma$ -CF<sub>2</sub>), 128 (2F,  $\delta$ -CF<sub>2</sub>), 124.6 (2F,  $\epsilon$ -CF<sub>2</sub>), 81.7 (3F, CF<sub>3</sub>). IR spectrum ( $\nu$ , cm<sup>-1</sup>): 1770 (C=O).</sub></sub>

3,3,4,4,5,5,6,6-Octafluoro-2,7-octanedione (VI). MeMgI was obtained from 25 g (1.04 moles) Mg and 149 g (1.04 moles) MeI in 300 ml ether. An additional 700 ml ether was added and the solution was cooled in a dry nitrogen stream to  $-78\,^{\circ}$ C. Then, a solution of 0.173 M perfluoroadipate diester in 200 ml ether cooled to  $-78\,^{\circ}$ C was added with rapid stirring over 3 min and the mixture was stirred for 7 h at the temperature indicated in Table 2. The reaction mass was decomposed with 75 ml concentrated hydrochloric acid in 80 ml ethanol such that the reaction temperature was not exceeded. Then, 250 ml water was added and the mixture was brought to 20°C. The ethereal layer was separated and washed with 100 ml saturated aq. K<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>SO<sub>3</sub>. The aqueous layers were combined and extracted with two 100-ml ether portions. The combined extracts were dried over MgSO<sub>4</sub>. Distillation gave (VI) with bp 178-180°C (748 mm). PMR spectrum ( $\delta$ , ppm): 2.36 (CH<sub>3</sub>). <sup>19</sup>F NMR spectrum ( $\delta$ , ppm): 122.2 (4F,  $\alpha$ -CF<sub>2</sub>), 123.9 (4F,  $\beta$ -CF<sub>2</sub>). IR spectrum ( $\nu$ , cm<sup>-1</sup>): 1770 (C=O).

Ethyl Ester of 3,3,4,4,5,5,6,6-Octafluoro-2-heptanone-6-carboxylic Acid (IV). MeMgI was obtained from 20.94 g (0.456 mole) Mg and 64.7 g (0.456 mole) MeI in 250 ml ether. The solution was cooled with rapid stirring in a nitrogen stream to  $-78^{\circ}$ C. A solution of 26.3 g (0.076 mole) diethyl ester of perfluoroadipic acid in 250 ml ether cooled to  $-78^{\circ}$ C was added with efficient stirring over 3 min. The mixture was brought to  $-45^{\circ}$ C and stirring was continued for 45 min. Then, the mixture was decomposed by the addition of 40 ml hydrochloric acid in 60 ml ethanol. The mixture obtained was washed with 50 ml saturated aq.  $K_2CO_3$  and  $Na_2SO_4$  and, then, 100 ml distilled water and dried over MgSO<sub>4</sub>. Distillation of the ether gave 28.83 g of a mixture of three compounds, two of which were identified as the diketone and diester by gas-liquid chromatography. <sup>1</sup>H and <sup>19</sup>F NMR spectroscopy indicated that the mixture contained 87% diketone, 2% diester, and 11% (IV). PMR spectrum of (IV) ( $\delta$ , ppm, J, Hz): 2.35 (COCH<sub>3</sub>), 1.25 t (CH<sub>3</sub>, J = 7), 4.33 q (CH<sub>2</sub>CH<sub>3</sub>). <sup>19</sup>F NMR spectrum of (IV) ( $\delta$ , ppm): 120.9 (2F, CF<sub>2</sub>CO<sub>2</sub>Et), 124.0 [(4F, CF<sub>2</sub>(CF<sub>2</sub>)<sub>2</sub>CF<sub>2</sub>], 122.2 (2F, CF<sub>2</sub>COCH<sub>3</sub>).

### CONCLUSIONS

In the reaction of methylmagnesium iodide with esters of perfluorocarboxylic acids, the magnesium salt of the hemiketal was found to be more stable and the ketone yield was found to be higher with increasing bulk of the alkoxy group of the ester.

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