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New Synthetic Approaches to 2-Perfluoroalkyl-4H-pyran-4-ones

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Abstract: A convenient synthesis of 5-substituted 2-perfluoroalkyl-4H-pyran-4-ones by dehydration of 2,3-dihydro-3-hydroxy-6-perfluoroalkyl-4H-pyran-4-ones is described. The 6-substituted and parent 2-perfluoroalkyl-4H-pyran-4-ones have been more successfully prepared using the condensation of alkyl enol ethers, derived from β-dicarbonyl compounds, with ethyl perfluoroalkanoates.

INTRODUCTION

Heterocyclic compounds containing perfluoroalkyl substituents have attracted much attention due to their remarkable biological activity, their specific chemical reactivity and physical properties. In particular, perfluoroalkylated six-membered heterocycles have important applications in medicinal[1] and agricultural[2] scientific fields, in host-guest chemistry,[3] and in the chemistry of laser dyes.[4] Therefore, the development of synthetic methodologies for the regioselective introduction of short-chain perfluoroalkyl groups into heterocyclic rings is of current interest.[1a,5]

Thus, a large number of fluoroalkyl substituted 4(1H)-pyridinones and especially pyridine derivatives are known.[1b,c,2c,6] At the same time, there are only a few reported 2-perfluoroalkyl-4H-pyran-4-ones,[7] which are suitable precursors of a variety of perfluoroalkylated nitrogen-containing heterocycles.[7c,d, 8]

In this paper, we describe our investigations directed toward the synthesis of the title compounds using the dehydration of 2,3-dihydro-3-hydroxy-6-perfluoroalkyl-4H-pyran-4-ones (**2**), which are easily prepared by condensation of 2-acetyloxiranes **1** with ethyl perfluoroalkanoates, as reported earlier by one of us (Scheme 1).[9] An alternative approach to the title pyranones, based on the condensation of ethyl perfluoroalkanoates with alkyl enol ethers derived from β-dicarbonyl compounds as common building blocks, is also proposed.

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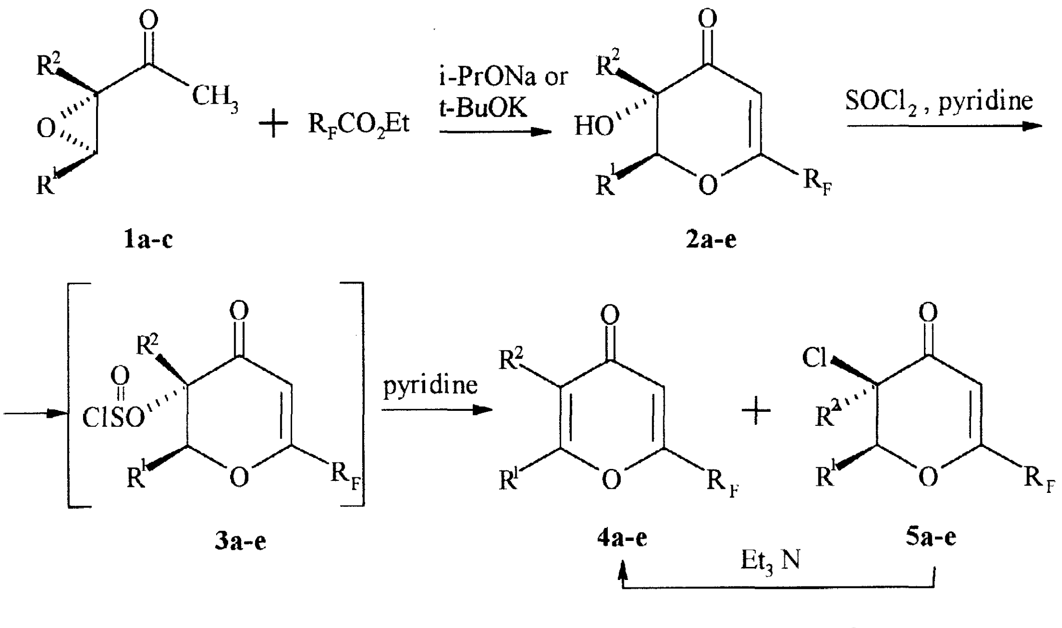
RESULTS AND DISCUSSION

The dehydration of hydroxy dihydropyranones **2** was performed by the action of a slight excess of thionyl chloride in dry pyridine, the desired methyl and phenyl substituted 2-perfluoroalkyl-4H-pyran-4-ones **4** being obtained in 61-79 % yield,[10] except pyranone **4c** which was prepared in poor isolated yield (Scheme 1). As TLC and ^{1}H NMR data showed, the crude substances **4a,b,d,e** were accompanied by 10-15 % of chlorine-containing compounds **5a,b,d,e**. The yield of these substitution products increased in the absence of base. Thus, treatment of hydroxy ketone **2a** with $SOCl_2$ at reflux in chloroform solution during 15 h resulted, after the usual workup, in the formation of a mixture of pyranone **4a** and chloride **5a** in a ratio of 3 : 2. Chloropyranones **5a,b** were isolated by column chromatography, and it was established that the dehydrochlorination of these compounds by the action of pyridine proceeded very sluggishly even under reflux. Taking this observation into account, it is believed that the pyranones **4a,b,d,e** are mainly formed immediately from the corresponding chlorosulfites **3**. At the same time, chlorides **5a,b** were easily converted into the target pyranones **4a,b** by heating in triethylamine. Our attempts to improve the yield of pyranones **4** in the reaction of compounds **2** with $SOCl_2$ using Et_3N instead of pyridine failed. Pure compounds **4a,b,d,e** were prepared in reproducible good yields by a combined procedure including the treatment of hydroxy pyranones **2 a,b,d,e**, dissolved in dry pyridine, with $SOCl_2$ followed by reflux of the crude products in an excess of dry Et_3N.

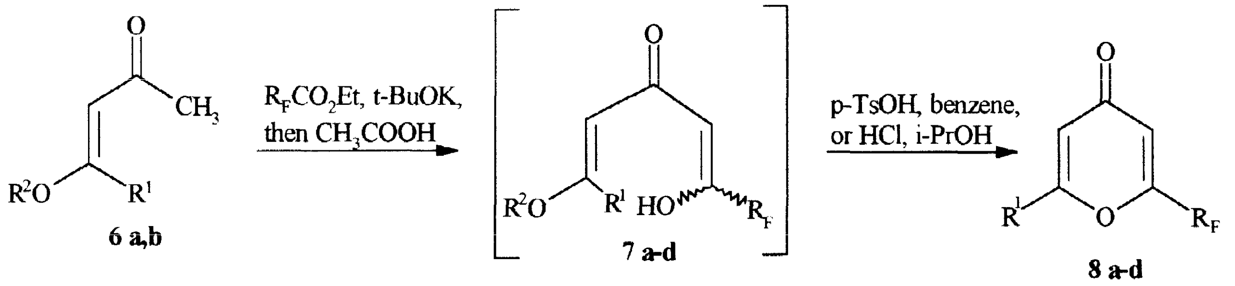


1-5 a,d R^1=H, R^2=CH_3; **b,e** R^1=H, R^2=Ph; **c** R^1=R^2=CH_3; **2-5 a-c** R_F=CF_3; **d,e** R_F=C_3F_7.

Scheme 1

The low yield of dimethyl substituted pyranone **4c** can be attributed to the unfavorable *cis*-arrangement of the hydroxy group and the hydrogen atom at position 2 in the substrate **2c**.[9] Allowing the solution of the latter compound in dry pyridine to stir with thionyl chloride for 8 h at room temperature probably produced chlorosulfite **3c**. Some amounts (about 10 %) of desired pyranone **4c** together with chloride **5c**[11] appeared upon additional stirring for 12 h at 60 °C. After workup of the reaction mixture with water followed by heating with Et_3N, large amounts of the starting hydroxy ketone **2c** were reformed, which can be easily explained by the sensitivity of intermediate **3c** to hydrolysis. In addition, side product **5c** is presumed to have the relative configuration as depicted in Scheme 1, in accordance with the observation that approximately the same reaction time is required for dehydrochlorination of compounds **5a,b,d,e** and **5c** (6 h *versus* 8 h, respectively).

Since 6-substituted pyranones of type **4c** could not be obtained in good yield *via* the above mentioned procedure, it was decided to develop an alternative approach to the synthesis of pyranones **8a-d**. For the preparation of these substances, the use of alkyl enol ethers **6** derived from *β*-dicarbonyl compounds as known suitable building blocks for various pyranones[12] proved to be successfull (Scheme 2).



6-8 a,c $R^1=CH_3$; **b,d** $R^1=H$; **6, 7 a,c** $R^2=Et$; **b,d** $R^2=CH_3$; **7, 8 a,b** $R_F=CF_3$; **c,d** $R_F=C_3F_7$.

Scheme 2

Thus, the reaction of acetylacetone enol ether **6a** with ethyl perfluoroalkanoates in the presence of an excess of potassium *tert*-butoxide, followed by acid catalyzed cyclization with *p*-TsOH in benzene, afforded the target 6-substituted pyranones **8a,c** in 75 and 57 % overall yield, respectively. Similarly, the parent compounds **8b,d** were obtained from the corresponding formylacetone derivative **6b** in a yield of 40 and 64 %, respectively. Arising after the condensation stage, intermediate enols **7a-d** without isolation were converted into compounds **8a-d**. The enols **7a-d** showed a significant difference in their reactivity in the cyclization step. Thus, for the transformation of enols **7b,d** ($R^1=H$) into the corresponding pyranones **8b,d**, more drastic conditions were required (HCl, boiling i-PrOH) as compared with the cyclization of **7a,c**.

The structures of all new synthesized pyranones **4** and **8** were confirmed by ^1H NMR, ^{13}C NMR and mass spectroscopy. In particular, the proton assignment in the spectrum of pyranone **4a** was made on the basis of a specific coupling between the methyl group protons at δ 1.83 (J=1.3 Hz) and the proton at C-6 appearing as a quartet at δ 7.76. The distinctive characteristic of the spectrum of the parent monosubstituted pyranone **8b** was a doublet of doublets at δ 6.35 (J=2.5, 5.8 Hz) and a set of two doublets at δ 6.67 ($J_{3,5}$=2.5 Hz) and δ 7.90 ($J_{5,6}$=5.8 Hz), accounting for the pyranone ring protons at C-5, C-3 and C-6, respectively. In the case of pyranone **8a**, the proton at C-5 appeared as a multiplet, whereas the proton at C-3 appeared as the doublet with a coupling constant $J_{3,5}$=2.31 Hz, which was similar to that for the parent **8b**. The spectra of the C_3F_7-substituted products **4d,e** and **8c,d** were essentially the same as those of their trifluoromethylated counterparts. The spectra of the chlorides **5a-c** resembled the spectra of the corresponding hydroxy precursors.[9]

In conclusion, a convenient two-step method for the preparation of 5-substituted 2-perfluoroalkyl-4H-pyran-4-ones starting from 2-acetyloxiranes was developed. Additionally, unsubstituted and 6-substituted 2-perfluoroalkyl-4H-pyran-4-ones have been prepared with β-dicarbonyl compounds alkyl enol ethers as building blocks.

EXPERIMENTAL

IR spectra were measured on a Specord 75 IR spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker AC-200 (200 MHz), a JEOL JNM-EX 270 (270 MHz) or a Tesla BS-467A (60 MHz) spectrometer. ^{13}C NMR spectra were recorded on a JEOL JNM-EX 270 (68 MHz) spectrometer. Chemical shifts are reported relative to internal Me_4Si. Mass spectra were recorded on a Shimadzu QP-5000 GC/MS spectrometer. Melting points were determined in open capillaries and are uncorrected. Preparative column chromatography was carried out on silica gel L Chemapol (40-100 Mesh). All chemicals were reagent grade while solvents were dried and distilled before use. 2-Acetyl-2-phenyloxirane **(1b)** was prepared as previously reported.[13] Hydroxy pyranones **2a,c,d** were synthesized by a known procedure,[9] and pyranones **2b,e** were prepared as given below. 4-Ethoxy-3-pentene-2-one **(6a)** was obtained by a literature method.[14]

Preparation of 2,3-dihydro-3-hydroxy-3-phenyl-6-(trifluoromethyl)-4H-pyran-4-one (2b). To a vigorously stirred suspension of potassium *tert*-butoxide (10.0 g, 89 mmol) in dry dimethoxymethane (170 mL) was added dropwise a mixture of 2-acetyloxirane **1b** (11.1 g, 68 mmol) and ethyl trifluoroacetate (9.7 mL, 82 mmol) at -15 °C over a period of 30 min. The stirred reaction mixture was gradually warmed to ambient temperature over 3 h, then cooled to 0 °C and quenched by careful addition of glacial acetic acid (5.3 mL, 89 mmol). After removal of dimethoxymethane under reduced pressure, the residue was treated with water (30 mL) and extracted with $CHCl_3$ (25 mL x 5). The organic phases were combined, washed with saturated aqueous $NaHCO_3$ solution and dried over Na_2SO_4. The solvent was evaporated and the residue was recrystallized to afford hydroxy pyranone **2b** (11.3 g, 65 %), m.p. 43.0-43.5 °C (pentane-Et_2O) ; IR (CCl_4) 3500, 1700, 1645 cm^{-1}; ^{1}H NMR (60 MHz, CCl_4) δ 4.38 and 4.84 (2 x d, J=12 Hz, 2H), 5.42 (br s, 1H), 5.70 (s, 1H), 7.27 (s, 5H). EIMS (70 eV) *m/z* (rel. int.) no M$^+$, 241 (M$^+$-OH, 1), 121 (9), 120 (100), 106 (5), 105 (70), 92 (5), 91 (22), 78 (64), 77 (43), 69 (12), 65 (9), 51 (23), 50 (9), 43 (9), 42 (4), 39 (10). Anal. Calcd for $C_{12}H_9F_3O_3$: C, 55.82; H, 3.51. Found: C, 55.97; H, 3.68.

2,3-Dihydro-6-(heptafluoropropyl)-3-hydroxy-3-phenyl-4H-pyran-4-one (2e) was synthesized in similar way as described for **2b** from oxirane **1b** (1.6 g, 10 mmol) and ethyl heptafluorobutyrate (2.1 mL, 12 mmol) to afford colourless crystals (2.2 g, 61 %): m.p. 84.5-85.0 °C (hexane); IR (CCl_4) 3505, 1705, 1640 cm^{-1}; ^{1}H NMR (60 MHz, CCl_4) δ 3.93 (br s, 1H), 4.36 and 4.88 (2 x d, J=12 Hz, 2H), 5.92 (s, 1H), 7.27 (s, 5H). Anal. Calcd for $C_{14}H_9F_7O_3$: C, 46.94; H, 2.53. Found: C, 47.06; H, 2.69.

General procedure for the dehydration of hydroxy pyranones 2a,b,d,e. To a stirred solution of pyranone **2a,b,d,e** (10 mmol) in dry pyridine (3.2 mL, 40 mmol) was added dropwise $SOCl_2$ (1 mL, 14 mmol) at -15 °C over 30 min. After stirring for 2 h at 0 °C and 3 h at room temperature, this mixture was cooled again to 0 °C and quenched by addition of crushed ice (5 g), then extracted with Et_2O (10 mL x 5). The combined organic phases were washed with 10 % HCl, then saturated aqueous $NaHCO_3$ solution, and dried over Na_2SO_4. After evaporation of the solvent, the resulting mixture was refluxed in triethylamine (5 mL) for 6 h. The amine was removed by rotary evaporation, the residue was treated with water (5 mL) and extracted with Et_2O (10 mL x 5). The organic phases were combined, washed with 10 % HCl, saturated aqueous $NaHCO_3$ solution and dried over Na_2SO_4. After evaporation of the solvent, the residue was distilled to obtain pyranone **4a**, crystallized to isolate **4b** or chromatographed on silica gel using $CHCl_3$ to obtain pyranones **4d,e**.

5-Methyl-2-(trifluoromethyl)-4H-pyran-4-one (4a): (71 %), b.p. 69-70 °C/ 14 mmHg, n_D^{20} 1.4401, m.p. 15 °C (pentane-Et_2O); IR (CCl_4) 1680, 1650 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.99 (s, 3H), 6.73 (s, 1H), 7.78 (s, 1H); (60 MHz, CCl_4) δ 1.83 (d, J=1.3 Hz, 3H), 6.53 (s, 1H), 7.76 (q, J=1.3 Hz, 1H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 10.89 (Me), 113.85 (d, J=2.4 Hz, $\underline{C}H{=}CF_3$), 118.45 (q, J=273.5 Hz, CF_3), 127.56 ($\underline{C}Me$), 151.43 ($\underline{C}H{=}CMe$), 152.96 (q, J=39.5 Hz, $\underline{C}CF_3$), 178.00 (C=O). EIMS (70 eV) *m/z* (rel. int.) 179 (M^++1, 7), 178 (M^+, 91), 150 (4), 149 (6), 139 (22), 131 (10), 119 (7), 102 (12), 101 (6), 81 (29), 75 (10), 69 (100), 56 (12), 55 (11), 53 (33), 41 (13), 40 (20), 39 (56). Anal. Calcd for $C_7H_5F_3O_2$: C, 47.20; H, 2.83. Found: C, 47.34; H, 3.01.

5-Phenyl-2-(trifluoromethyl)-4H-pyrane-4-one (4b): (61 %), m.p. 139.5-140.0 °C (toluene); IR (CCl_4) 1680, 1650 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 6.81 (s, 1H), 7.39-7.49 (m, 5H, C_6H_5), 7.91 (s, 1H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 115.65 (s, $\underline{C}H{=}CCF_3$), 118.36 (q, J=273.4 Hz, CF_3), 128.70 and 128.73 (HC_{ortho} and HC_{meta} or *vice versa*), 129.22 (HC_{para}), 129.83 and 130.92 (2 x C_{quat}), 152.27 (s, $\underline{C}CF_3$), 152.43 ($\underline{C}H{=}CPh$), 175.92 (C=O). EIMS (70 eV) *m/z* (rel. int.) 241 (M^++1, 5), 240 (M^+, 43), 239 (40), 193 (3), 189 (1), 164 (1), 143 (1), 133 (2), 115 (4), 103 (8), 102 (100), 95 (11), 89 (7), 76 (15), 75 (7), 74 (5), 69 (6), 63 (12), 62 (5), 52 (6), 51 (8), 50 (8), 39 (9). Anal. Calcd for $C_{12}H_7F_3O_2$: C, 60.01; H, 2.94. Found: C, 60.12; H, 3.08.

2-(Heptafluoropropyl)-5-methyl-4H-pyrane-4-one (4d): (79 %), b.p. 85 °C/ 15 mmHg, n_D^{20} 1.4020, m.p. 13-14 °C, IR (CCl_4) 1670, 1645 cm^{-1}; ^{1}H NMR (60 MHz, CCl_4) δ 1.82 (d, J=1.3 Hz, 3H), 6.66 (s, 1H), 7.85 (q, J=1.3 Hz, 1H). EIMS (70 eV) *m/z* (rel. int.) 279 (M^++1, 3), 278 (M^+, 19), 251 (1), 239 (16), 131 (10), 87 (8), 81 (2), 75 (7), 69 (29), 57 (6), 56 (4), 55 (6), 53 (7), 43 (100), 41 (8), 40 (5), 39 (19). Anal. Calcd for $C_9H_5F_7O_2$: C, 38.87; H, 1.81. Found: C, 38.98; H, 1.93.

2-(Heptafluoropropyl)-5-phenyl-4H-pyran-4-one (4e): (75 %), m.p. 99.5-100.0 °C (toluene); IR (CCl_4) 1680, 1655 cm^{-1}; ^{1}H NMR (60 MHz, $CDCl_3$) δ 6.77 (s, 1H), 7.33 (s, 5H), 7.83 (s, 1H). Anal. Calcd for $C_{14}H_7F_7O_2$: C, 49.43; H, 2.07. Found: C, 49.58; H, 2.19.

5,6-Dimethyl-2-(trifluoromethyl)-4H-pyran-4-one (4c). To a stirred solution of hydroxy pyranone **2c** (3.8 g, 18 mmol) in dry pyridine (5.8 mL, 72 mmol) was added $SOCl_2$ (1.8 mL, 25 mmol) at -5 °C over a period of 25 min. After the addition was completed, the mixture was stirred for 2 h at 0 °C and for 12 h at 60 °C. Then it was cooled to 0 °C, diluted with ice-cold water (10 mL) and extracted with Et_2O (10 mL x 5). The organic phases were combined, washed with 10 % HCl, saturated aqueous $NaHCO_3$ solution, and dried over Na_2SO_4. Evaporation of the solvent gave the mixture (2.4 g) of starting material **2c**, pyranone **4c** and chloride **5c**, which was then refluxed in triethylamine (10 mL) for 8 h. After the standard workup as described above, the residue (2.1 g) was chromatographed on silica gel using hexane-chloroform (1:1) eluent. The desired pyranone **4c** (0.8 g, 23 %) and starting hydroxy pyranone **2c** (1.2 g) were subsequently isolated. **4c**: b.p. 93 °C/ 22 mmHg; m.p. 27-28 °C; n_D^{20} 1.4471; IR (CCl_4) 1670, 1640, 1615 cm^{-1}; ^{1}H NMR (60 MHz, CCl_4) δ 1.79 (s, 3H), 2.28 (s, 3H), 6.58 (s, 1H). EIMS (70 eV) *m/z* (rel. int.) 193 (M^++1, 10), 192 (M^+, 100), 165 (2), 163 (11), 149 (15), 139 (60), 123 (6), 119 (15), 97 (9), 96 (7), 95 (34), 83 (14), 81 (11), 75 (8), 69 (95), 67 (27), 55 (34), 54 (91), 53 (57), 50 (22), 41 (45), 40 (9), 39 (90). Anal. Calcd for $C_8H_7F_3O_2$: C, 50.01; H, 3.67. Found: C, 50.17; H, 3.78.

3-Chloro-2,3-dihydro-3-methyl-6-(trifluoromethyl)-4H-pyran-4-one (5a). The residue from the reaction of dihydropyranone **2a** (1.7 g, 9 mmol) with $SOCl_2$ (0.9 mL, 13 mmol) in pyridine (3.0 mL, 37 mmol) under the conditions described for **4a** preparation, but without treatment with Et_3N, was submitted to column chromatography (SiO_2, $CHCl_3$), providing subsequently the chloride **5a** (0.2 g, 10 %) and pyranone **4a** (1.0 g, 62 %). **5a**: b.p. 65-67 °C/ 11 mmHg; n_D^{20} 1.4379; IR (CCl_4) 1710, 1650 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.70 (s, 3H), 4.44 and 4.72 (2 x d, J=13 Hz, 2H), 5.95 (s, 1H). EIMS (70 eV) *m/z* (rel. int.) 214/6 (M^+, 3), 186/8 (5), 139 (40), 119 (4), 103 (3), 76/8 (82), 69 (41), 53 (6), 41 (100), 40 (15), 39 (41). Anal. Calcd for $C_7H_6ClF_3O_2$: C, 39.18; H, 2.82. Found: C, 39.25; H, 2.89.

3-Chloro-2,3-dihydro-3-phenyl-6-(trifluoromethyl)-4H-pyran-4-one (5b) was obtained (0.3 g, 15 %) along with pyranone **4b** (0.8 g, 48 %) in similar way as described for the synthesis of compound **5a** starting from dihydropyranone **2b** (1.9 g, 7 mmol. **5b**: m.p. 46.0-46.5 °C (pentane); IR (CCl_4) 1715, 1655 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 4.74 and 5.00 (2 x d, J=12.54 Hz, 2H, CH_2O), 6.01 (s, 1H, $CH=CCF_3$), 7.39-7.53 (m, 5H, C_6H_5). ^{13}C NMR (68 MHz, $CDCl_3$) δ 66.97 (CCl), 76.51 (CH_2O), 103.54 (s, $\underline{C}H=CCF_3$), 118.32 (q, J=275 Hz, CF_3), 127.20 and 128.98 (HC_{ortho} and HC_{meta} or *vice versa*), 129.81 (HC_{para}), 133.40 (=$\underline{C}$-CCl), 158.16 (q, J=37.9 Hz, $\underline{C}CF_3$), 185.59 (C=O). Anal. Calcd for $C_{12}H_8ClF_3O_2$: C, 52.10; H, 2.91. Found: C, 52.23; H, 3.08.

Preparation of pyranones 8a-d. To a vigorously stirred suspension of potassium *tert*-butoxide (1.5 g, 13 mmol) in dry Et_2O (25 mL) was added dropwise the mixture of enol ether **6a** or **6b** (10 mmol) and the corresponding ethyl perfluoroalkanoate (12 mmol) at -15 °C over 30 min. After the addition was completed, the stirred reaction mixture was allowed to warm gradually to room temperature over 3 h. Then it was cooled to 0 °C, quenched by subsequent dropwise addition of glacial acetic acid (0.8 mL, 13 mmol) and water (5 mL). The aqueous layer was separated and extracted with Et_2O (10 mL x 5). The combined organic phases were washed with saturated aqueous $NaHCO_3$ solution and dried over Na_2SO_4. To obtain pyranones **8a,c** the residue after Et_2O removal was refluxed in dry benzene (25 mL) for 10 h in the presence of catalytic amounts of *p*-TsOH (0.5 mmol). The cooled benzene solution was washed with $NaHCO_3$ and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was distilled to afford pyranones **8a,c.** For the preparation of pyranones **8b,d**, the residue after removal of Et_2O was dissolved in i-PrOH (20 mL), then 35 % aqueous HCl (0.25 mL) was added and the resulting solution was refluxed for 45 min. After evaporation of i-PrOH, the residue was distilled to obtain pyranones **8b,c**.

6-Methyl-2-(trifluoromethyl)-4H-pyran-4-one (8a): (75 %), b.p. 85-86 °C/ 15 mmHg, m.p. 49-50 °C (pentane); IR (CCl_4) 1680, 1650, 1625 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 2.38 (s, 3H, Me), 6.25 (m, 1H, C$\underline{H}$=CMe), 6.64 (d, J=2.31 Hz, 1H, CH=CF_3). ^{13}C NMR (68 MHz, $CDCl_3$) δ 19.73 (Me), 114.52 (d, J=2.5 Hz, $\underline{C}$H=CCF_3), 115.90 ($\underline{C}$H=CMe), 118.61 (q, J=274 Hz, CF_3), 152.78 (q, J=39.5 Hz, $\underline{C}CF_3$), 166.54 ($\underline{C}$Me), 177.91 (C=O). EIMS (70 eV) *m/z* (rel. int.) 178 (M^+, 16), 150 (4), 149 (8), 139 (2), 131 (6), 119 (3), 113 (3), 111 (3), 109 (2), 99 (6), 95 (5), 85 (13), 84 (5), 83 (10), 82 (5), 81 (18), 69 (70), 53 (16), 43 (100), 42 (18), 40 (12), 39 (26). Anal. Calcd for $C_7H_5F_3O_2$: C, 47.20; H, 2.83. Found: C, 47.31; H, 2.95.

2-(Trifluoromethyl)-4H-pyran-4-one (8b): (40 %), b.p. 71-73 °C/ 13 mmHg, n_D^{20} 1.4402, m.p. 21-22 °C (pentane-Et_2O); IR (CCl_4) 1680, 1645, 1635 cm^{-1}; ^1H NMR (60 MHz, CCl_4) δ 6.35 (dd, J=5.8, 2.5 Hz, 1H), 6.67 (d, J=2.5 Hz, 1H), 7.90 (d, J=5.8 Hz, 1H). EIMS (70 eV) *m/z* (rel. int.) 164 (M^+, 10), 163 (100), 144 (16), 136 (4), 135 (7), 115 (5), 94 (76), 75 (7), 69 (22), 53 (10), 42 (15), 41 (10), 39 (9). Anal. Calcd for $C_6H_3F_3O_2$: C, 43.92; H, 1.84. Found: C, 44.01; H, 1.96.

2-(Heptafluoropropyl)-6-methyl-4H-pyrane-4-one (8c): (57 %), b.p. 91-92 °C/ 11 mmHg; m.p. 64.5-65.0 °C (hexane), IR (CCl_4) 1680, 1645, 1615 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 2.36 (d, J=1 Hz, 3H, Me), 6.25 (q, J=1 Hz, 1H, C$\underline{H}$=CMe), 6.68 (d, J=2.31 Hz, 1H, CH=CCF_2). ^{13}C NMR (68 MHz, $CDCl_3$) δ 19.71 (Me), 108.54 (q x t, J=36, 268 Hz, CF_3), 110.30 (t x t, J=259, 31 Hz, $\underline{C}F_2CF_2CF_3$), 115.99 ($\underline{C}$H=CMe), 117.00 (t, J=3.7 Hz, $\underline{C}$H=CCF_2), 117.67 (t x q, J=33 , 288 Hz, $CF_2\underline{C}F_2CF_3$), 152.94 (t, J=30 Hz, $\underline{C}CF_2$), 166.72 ($\underline{C}$Me), 177.61 (C=O). Anal. Calcd for $C_9H_5F_7O_2$: C, 38.87; H, 1.81. Found: C, 38.99; H, 1.91.

2-(Heptafluoropropyl)-4H-pyran-4-one (8d): (64%), b.p. 81-83 °C/ 11 mmHg; m.p. 34.0-34.5 °C (pentane); IR (CCl_4) 1680, 1650 cm^{-1}; ^1H NMR (60 MHz, CCl_4) δ 6.23 (d x d, J=5.8, 2.5 Hz, 1H), 6.53 (d, J=2.5 Hz, 1H), 7.69 (d, J=5.8 Hz, 1H). **EIMS** (70 eV) *m/z* (rel. int.) 265 (M^++1, 3), 264 (M^+, 33), 245 (1), 217 (5), 175 (2), 118 (3), 117 (57), 100 (2), 95 (1), 75 (8), 70 (23), 69 (100), 53 (6), 42 (18), 41 (17), 39 (10). **Anal.** Calcd for $C_8H_3F_7O_2$: C, 36.38; H, 1.14. **Found**: C, 36.52; H, 1.31.

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11. Chloride **5c** was not isolated in pure state. Its ^1H NMR data were obtained from the spectrum of the reaction mixture and were as follows: (60 MHz, CCl_4) δ 1.48 (s, 3H), 1.55 (d, J=6.2 Hz, 3H), 4.32 (q, J=6.2 Hz, 1H), 5.81 (s, 1H).
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