Experimental Section

Melting points were taken in vacuo, corrected. $[\alpha]^{25}_D$ values are measured in 3% in $CHCl_3$ unless otherwise stated. IR spectra were take in 2.5% in CS_2 or $CHCl_3$ and ^1H NMR spectra at 60 MHz in $CDCl_3$. ^{13}C NMR was recorded at 15 °C in $CDCl_3$ solution on a Bruker WM-250 Fourier transform spectrometer at 63 MHz. Chemical shifts (±0.1 ppm) are given with respect to Me_4Si, used as an internal standard. Mass spectra were taken with a Varian MAT 311A (direct inlet, 70 eV). t_r values of cholesteryl derivatives (5% OV-101, 250 °C) were as follows: Δ^0, 1.00; Δ^5, 1.00; $\Delta^{5,22E}$, 0.91; $\Delta^{5,24}$, 1.07; $\Delta^{5,25}$, 1.07; $\Delta^{5,22E,24}$, 1.14. R_f values of cholesteryl derivatives acetate (TLC system 1, 10% $AgNO_3$-silica gel plates, 5:2 hexane–benzene, 4-h development[15]) were as follows: Δ^0, 1.22; Δ^5, 1.00; $\Delta^{5,22E}$, 0.65; $\Delta^{5,24}$, 0.51; $\Delta^{5,22E,24}$, 0.28; $\Delta^{5,25}$, 0.17. R_f values of **2** acetoxy alcohols (TLC system 2, silica gel, 6:4 hexane–EtOAc one development) were as follows: **3**, 0.54; **6**, 0.48.

(20*S*,22*R*,*S*)-3β-Acetoxychola-5,23-dien-22-ol (2). Freshly prepared 0.97 M vinylmagnesium bromide[24] in 80 mL of THF was added dropwise over 10 min to a stirred solution of 18 g of **1** (mp 114–116.5 °C)[25] in 150 mL of THF on an ice bath. The mixture was stirred an additional 10 min and then poured into 200 mL of 1 N HCl. The products were extracted with ether, the ether layer was washed with H_2O, dried over Na_2SO_4, and evaporated, and the residue was chromatographed on Florisil with 3:1 CH_2Cl_2–petroleum ether (p.e.) to yield 12.8 g (66%) of **2** as a 22*R* and 22*S* mixture, single peak on GLC, t_r 0.91, two components on TLC (system 2), R_f 0.54 and 0.48 in a ratio of ca. 4:1.

(22*S*)-3β-Acetoxychola-5,23-dien-22-ol (3). The 22*R*,*S* mixture **2** was placed on 100 parts of 2:1 silica gel–Celite and eluted with 9:1 p.e.–ether and the R_f 0.54 material purified by crystallization from hexane: mp 163.5–165 °C, $[\alpha]^{25}_D$ −83.3°; IR 3610 (OH), 1730, 1240 (OAc), 1133, 1028, 980, 920, 840 cm^{-1}; ^1H NMR δ 0.70 (3 H, s, C18), 0.95 (3 H, d, C21), 1.02 (3 H, s, C19), 2.02 (3 H, s, CH_3CO), 2.32 (2 H, d, C4), 4.25 (1 H, br, C22), 4.70 (1 H, br, C3α), 5.02 and 5.19 (2 H, two q, C24), 5.32 (1 H, m, C6), 5.96 (1 H, octet, C23); ^{13}C NMR δ 52.17 (C17), 11.87 (C18), 40.98 (C20), 11.78 (C21), 74.28 (C22), 139.71 (C23), 113.62 (C24); mass spectra; *m*/*e* (relative intensity) 340 (M − HOAc, 49), 283 (M − HOAc − C_3H_5O, C20–C22 cleavage, 52), 80 (100), 159, 145, 133, 119, 107, 105, 95, 93, 91, 78, 67, 55, 44, and 43 (21–49). Anal. Calcd for $C_{26}H_{40}O_3$: C, 77.95; H, 10.06. Found: C, 77.86; H, 10.35.

Horeau analysis:[17] $[\alpha]^{25}_D$ −6.7° (C16, $CHCl_3$), 21% optical yield, 22*S*.

Acetoxy alcohol **3** was hydrolyzed to the 22*S* 3β,22-diol **4**, mp 205.5–206.5 °C (from acetone), $[\alpha]^{25}_D$ −99.5° (*c* 3, pyridine), and acetylated to the (22*S*) 3β,22-diacetate (**5**), mp 153–154.5 °C (from MeOH), $[\alpha]^{25}_D$ −83.6°.

(22*R*)-3β-Acetoxychola-5,22-dien-22-ol (6). When the 22*R*,*S* mixture **2** was crystallized from 5% benzene–hexane and ether, the more polar fraction, R_f 0.48, was concentrated in the crystals. Elution of this material from 300 parts of alumina with 9:1 p.e.–ether yielded **6**: mp 204–205 °C (from $CHCl_3$); $[\alpha]^{25}_D$ −37.4°; IR 3610 (OH), 1730, 1240 (OAc), 988, 922, 900 cm^{-1}; ^1H NMR similar to **3** except δ 0.97 (3 H, d, C21), 5.05 and 5.25 (2 H, two d, C24), 5.89 (1 H, octet, C23); ^{13}C NMR δ 52.95 (C17), 12.41 (C18), 41.86 (C20), 12.41 (C21), 74.84 (C22), 137.09 (C23), 116.20 (C24); mass spectra, identical with that of **3**. Anal. Calcd for $C_{26}H_{40}O_3$: C, 77.95; H, 10.06. Found: C, 77.86; H, 10.11.

Horeau analysis:[17] $[\alpha]^{25}_D$ +1.4° (*c* 18, $CHCl_3$), 4.5% optical yield, 22*R*.

Acetoxy alcohol **6** was hydrolyzed to the 22*R* 3β,22-diol **7**, mp 211.5–212.5 °C (from acetone), $[\alpha]^{25}_D$ −2.4° (*c* 3, pyridine), and acetylated to the 22*R* 3β,22-diacetate **8**, mp 173.5–174.5 °C (from MeOH), $[\alpha]^{25}_D$ −27.4°.

Hydrogenations of 22-Dehydrodesmosterol. Reduction of 100–300 mg of 22-dehydrodesmosterol or its acetate[15] with H_2 at room temperature was done in a flask over a magnetic stirrer attached to a hydrogen buret. Diimide reductions with hydrazine and *p*-tosyl hydrazide were at 80–110 °C. Samples were removed periodically for GC and acetylated, if necessary, for $AgNO_3$–silica gel TLC. Representative results of 38 experiments are given in Table I.

25-Dehydrocholesteryl Acetate (13). The previous preparation[15] was scaled-up and simplified. A solution of 10 g of **2** and 40 mL of 1-(dimethylamino)-1-methoxy-1-propene in 180 mL of benzene was refluxed under N_2 for 2 h and allowed to stand overnight. It was washed with water several times, dried over Na_2SO_4, and evaporated to dryness and the residue chromatographed on 350 g of 2:1 silica gel (Mallinckrodt, 100 mesh)–celite with 4:1 p.e.–ether to give 11.1 g (92%) of 25*R*,*S* $\Delta^{5,22}$ amide **9**, which was directly hydrogenated in 500 mL of EtOAc over 0.4 g of PtO_2 until H_2 absorption ceased. The catalyst and solvent were removed, and the residual Δ^5 amide **10** was dissolved in 160 mL of THF and added dropwise to a refluxing slurry of 8 g of $LiAlH_4$ in 250 mL of THF over 1 h. The mixture was refluxed an additional 30 min, most of the THF removed at atmospheric pressure, and the residue decomposed with moist ether and a minimal amount of water. The ether was decanted from the white $LiAl(OH)_4$ sludge and evaporated and the residual amine **11** refluxed directly with 18 mL of 30% H_2O_2 in 250 mL of MeOH overnight. The solution was evaporated in vacuo (<45 °C) to a syrup that was extracted with p.e. and was dried from 100% EtOH to leave 11.4 g of *N*-oxide **12** (theoretical yield, 11.1 g). It was dissolved in 300 mL of pyridine and pyrolyzed by stirring the solution with 10 g of KOH in 105 °C oil bath for 3.5 h. After removal of most of the pyridine in vacuo, the residue was mixed with 400 mL of 1 N HCl, and the product was extracted with ether and chromatographed on 500 g 2:1 silica gel–celite with 9:1 p.e.–ether to give 6.9 g of 25-dehydrocholesterol. This was acetylated (Ac_2O–py) and crystallized from MeOH to give 7.4 g of **13**, mp 111.5–113 °C (lit.[3-5,15] mp 112–114 °C), in 69% yield from **2**.

Desmosteryl Acetate (14). A solution of 4.00 g of **13** and 0.64 g of I_2 in 800 mL benzene was refluxed overnight, cooled, washed with 1% $Na_2S_2O_3$ and water, evaporated, and the residue was chromatographed on a 500 g of 20% $AgNO_3$ 2:1 silica gel–celite column with 3:7 benzene–hexane to yield 3.33 g (83%) of **14**, 0.08 g of mixed fractions, and 0.47 g (11%) of **13**. **14**: mp 94–95 °C (from MeOH), $[\alpha]^{25}_D$ −42.4° (lit. 92.5–93 °C, −40.6°;[4] 96–97 °C, −43°[5]).

Desmosterol (15). Acetate **14** was hydrolyzed and desmosterol crystallized from MeOH: mp 121.5–122.5 °C, $[\alpha]^{26}_D$ −38.5° (lit. 120.5–121 °C, −39.2°;[4] 121–122 °C, −41°[5]).

Acknowledgment. We thank Dr. Robert Bates, Chemistry Department, University of Arizona, for assistance with ^{13}C NMR spectra and the National Science Foundation (Grant DEB-8207056) for partial support of this work.

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Synthesis of Fluoro Ethers with Acetyl Hypofluorite

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Received October 31, 1986

Since its first synthesis about six years ago, acetyl hypofluorite (AcOF) has become a popular fluorinating agent.[1] Its developing chemistry includes reactions with aromatic mercury derivatives including estrone[2] and also simple aromatic compouds, using particularly AcO^{18}F for

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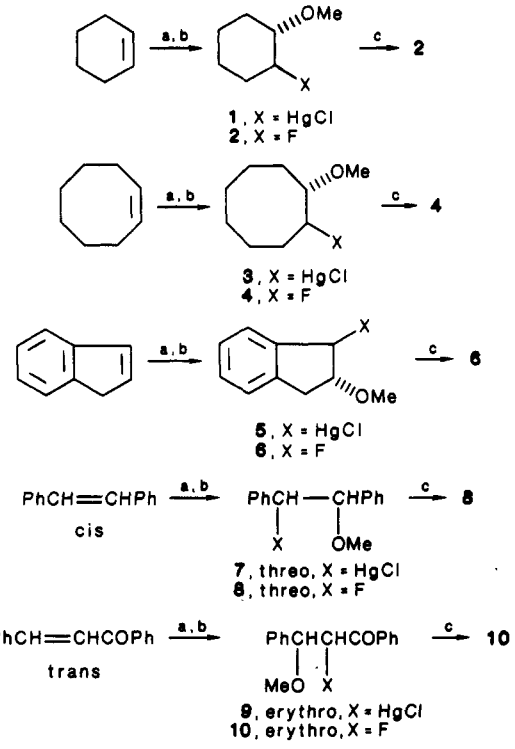
0022-3263/87/1952-2588$01.50/0

Scheme I[a]



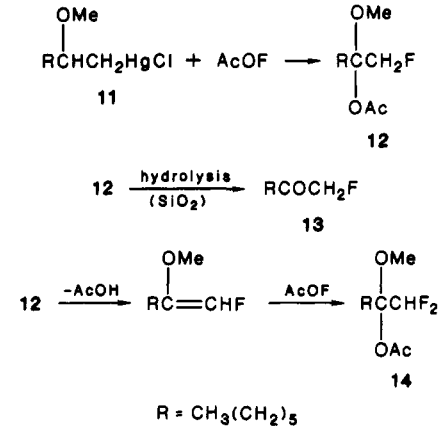
[a] (a) $Hg(OAc)_2$/MeOH; (b) NaCl; (c) AcOF.

positron emitting tomography.[3] We show in this note that AcOF can also react with nonaromatic mercury derivatives and substitute the metal via a rare front-side attack which results in full retention of configuration.

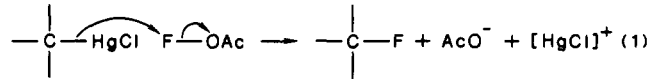
Olefins react with mercuric acetate in methanol via the trans addition of the elements of HgOAc and OMe. Treating this adduct with NaCl usually gives the corresponding crystalline RHgCl derivative in better than 80% yield.[4] When *trans*-1-methoxy-2-(chloromercurio)cyclohexane (**1**) was added to AcOF solution at −78 °C, *trans*-2-fluoro-1-methoxycyclohexane (**2**)[5] was produced in a quick reaction in 90% yield (Scheme I). The trans configuration was evidenced, among other things, from the coupling constants of ^1H and ^{19}F NMR spectra (see Experimental Section). Not all organomercury derivatives, however, reacted with the same ease at −78 °C. Larger ring compounds such as 2-(chloromercurio)-1-methoxycyclooctane (**3**) for example, reacted successfully with AcOF only at room temperature to produce 2-fluoro-1-methoxycyclooctane (**4**), still in very good yield. In such cases, however, a reverse addition of AcOF to the substrate is preferable (method B—see Experimental Section).

trans-1-(Chloromercurio)-2-methoxyindan (**5**), obtained from indene, reacted with AcOF at 0 °C, again with full retention of configuration, forming *trans*-2-methoxy-1-fluoroindane (**6**) in 80% yield.[6] Conjugated double bonds after mercuration also proved to be suitable substrates, and the fluorine atom replaced the metal again with a full retention of configuration. *cis*-Stilbene can serve as an example. It produced the anti adduct *threo*-1-(chloromercurio)-2-methoxy-1,2-diphenylethane (**7**), which was then converted in 75% yield to the known *threo*-1-fluoro-2-methoxy-1,2-diphenylethane (**8**).[7] The reaction was also tested for enones and the mercury derivative of benzalacetophenone (**9**), produced *erythro*-1,3-diphenyl-1-fluoro-2-methoxy-3-propanone (**10**) in good yield.

Scheme II



The retention of configuration for the transformation of the C–Hg bond to the C–F one is typical of electrophilic substitution at a saturated center.[8] It resembles in this respect the substitution of an unactivated tertiary hydrogen by fluorine.[9] This suggests that electrophilic fluorination involves a nucleophilic attack by the most electron-rich bond on the fluorine atom attached to a good leaving group.[10]



Terminal olefins, such as 1-octene, from which 1-(chloromercurio)-2-methoxyoctane (**11**) is formed, behave somewhat differently. Two main compounds were initially formed. Spectroscopic evidences point that the major component is 2-acetoxy-2-methoxy-1-fluorooctane (**12**), which after short absorption on silica gel column was transformed to 1-fluoro-2-octanone (**13**) in an overall yield of 44%[11] (Scheme II). The minor component, which proved to be 2-acetoxy-2-methoxy-1,1-difluorooctane (**14**), was stable toward chromatography and mild acidic conditions. We do not have at this point solid evidences for the intermediate of the **11** → **12** transformation although the facts that the elimination of AcOH, which has also been observed in previous cases,[12] is easier than the elimination of MeOH and that the oxygen atoms in **14** are less basic than in **12**, fully explain the formation and the stability of **14**. It should also be noted that $C_6H_5C_6H_4COCHF_2$ was obtained through a similar mechanism, when the enol acetate of biphenyl methyl ketone was reacted with fluoroxy reagents.[13]

In conclusion, this work presents a novel method for the synthesis of fluoro ethers, for which up to now a general method of preparation has been lacking. It should be noted that this is in sharp contrast to the many methods developed for the synthesis of the related fluorocarbonyl[14]

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and fluorohydrin[15] derivatives. Since these latter compounds can also be prepared with the aid of acetyl hypofluorite this reagent seems to be quite versatile and useful in organic chemistry. What is more, unlike the characteristic syn addition reactions of AcOF to double bonds, this work opens a way for the anti addition of the elements of fluorine and oxygen across olefins. Last, but not least, is the possibility of introducing the ^{18}F radioisotope by using the relatively easily labeled $AcO^{18}F$,[1d] and since the reactions described above are quite fast, this method could be very useful for preparation of fluoro ethers suitable for positron emitting tomography.

Experimental Section

^1H NMR spectra were recorded with a Bruker WH-90 and a Bruker WH-360 spectrometers at 90 and 360 MHz, respectively, with $CDCl_3$ as a solvent and Me_4Si as an internal standard. The ^{19}F spectra were measured at 84.67 and 338.8 MHz, respectively, and are reported in parts per million upfield from $CFCl_3$, which also served as internal standard. Mass spectra were measured with a Du Pont 21-491B spectrometer. IR spectra were recorded as neat films, in $CHCl_3$ solution or in KBr pellets on a Perkin-Elmer 177 spectrometer.

Preparation of the Mercury Derivatives. The appropriate olefin (10% excess) and $Hg(OAc)_2$ were mixed in MeOH at room temperature until no more precipitation of HgO occurred when NaOH was added. A saturated NaCl solution was then added, and the solid was filtered and recrystallized from MeOH.[4]

General Fluorination Procedure. A description of the setup and the procedure for working with elemental fluorine have previously been described.[14] It is worth repeating that F_2 and AcOF should be treated with care since they are strong oxidizers. The work should be conducted in an efficient hood or in a well-ventilated area. The toxicity of AcOF is not yet known, but some fluoroxy reagents are suspected to be strong poisons. If elementary precautions are taken, work with fluorine and its derivatives is safe and relatively simple.

Preparation of AcOF and methods of reaction were described in our work dealing with aromatic fluorinations.[1b] Two methods of addition were used. Method A consists of the addition of a cold $CHCl_3$ solution of the olefin to the AcOF solution, while in method B the oxidizing solution of AcOF was added dropwise with the aid of a pipet to the cold alkene solution so that the progress of the reaction could be monitored. In general the latter method resulted in a cleaner products. The reactions were usually carried out on scales of 10–40 mmol using 1.5–3 fold excess of AcOF, and, unless otherwise stated, the conversions were higher than 95%. The term "worked up as usual" means stopping the reaction by pouring it into 500 mL of water, washing the organic layer with $NaHCO_3$ solution followed by water until neutral, drying the organic layer over $MgSO_4$, and finally evaporating the solvent. The crude product was usually purified by vacuum flash chromatography using silica gel 60-H (Merck) and if needed also by HPLC (Waters) on Merck's LiChrosorb Si-100. Unless a melting point is given, the products are liquids.

Fluorination of 1 was carried out according to method A using 10 mmol of the mercury derivative and 20 mmol of AcOF at −78 °C. After 5 min, the reaction being complete and worked up as usual was flash chromatographed by using 5% EtOAc in petroleum ether as eluent. *trans*-2-Fluoro-1-methoxycyclohexane (**2**)[5] was thus isolated as an oil in 90% yield: NMR δ 4.30 (1 H, dm, J = 51 Hz, $W_{h/2}$ = 30 Hz), 3.41 (3 H, s); ^{19}F NMR −188.4 ppm (br d, J = 51 Hz).

Fluorination of 3 was carried out on 10 mmol at room temperature according to method B using 15 mmol of AcOF. The crude reaction mixture was flash chromatographed by using 5% EtOAc in petroleum ether as eluent. The fluoro ether **4** was thus isolated as an oil in 90% yield: NMR δ 4.64 (1 H, dm, J = 48 Hz), 3.50 (1 H, m), 3.42 (3 H, s), 2.2–1.2 (12 H, m); ^{19}F NMR −168.7 ppm (m). Anal. Calcd for $C_9H_{17}FO$: C, 67.50; H, 10.62. Found: C, 67.38; H, 10.49.

Fluorination of 5 was carried out on 10 mmol at 0 °C according to method B using 15 mmol of AcOF. The crude reaction mixture was flashed chromatographed by using 5% EtOAc in petroleum ether as eluent. The fluoro ether **6**[6] was thus isolated as an oil in 80% yield: NMR δ 7.35 (4 H, m), 5.90 (1 H, dd, J_1 = 57 Hz, J_2 = 4 Hz), 4.29 (1 H, m), 3.50 (3 H, s), 2.92 (2 H, m); ^{19}F NMR −178.0 ppm (dd, J_1 = 57 Hz, J_2 = 4 Hz).

Fluorination of 7 was carried out on 8 mmol according to method A using 30 mmol of AcOF. No reaction took place at −78 °C, but the starting material was fully consumed when the reaction mixture was allowed to warm up to 0 °C. After flash chromatography using 10% EtOAc in petroleum ether as eluent the fluoro ether **8**[7] was isolated as an oil in 75% yield: NMR δ 7.10 (10 H, m), 5.47 (1 H, dd, J_1 = 47 Hz, J_2 = 6.8 Hz), 4.46 (1 H, dd, J_1 = 14 Hz, J_2 = 6.8 Hz), 3.31 (3 H, s); ^{19}F NMR −180.74 ppm (dd, J_1 = 47 Hz, J_2 = 14 Hz).

Fluorination of 9 was carried out on 10 mmol according to method A using 20 mmol of AcOF. No reaction took place at −78 °C, but the starting material was fully consumed when the reaction mixture was allowed to warm up to 0 °C. After flash chromatography using 10% EtOAc in petroleum ether as eluent the fluoro ether **10** was isolated as an oil in 80% yield: IR 1685 cm^{-1}; NMR δ 6.5–7.20 (10 H, m), 5.40 (1 H, dd, J_1 = 50 Hz, J_2 = 3.5 Hz), 4.72 (1 H, dd, J_1 = 24 Hz, J_2 = 3.5 Hz), 3.23 (3 H, s); ^{19}F NMR −198.73 ppm (dd, J_1 = 50 Hz, J_2 = 24 Hz). Anal. Calcd for $C_{16}H_{25}FO_2$: C, 74.42; H, 5.81. Found: C, 74.70; H, 5.92.

Fluorination of 11 was carried out on 10 mmol according to method A using 30 mmol of AcOF. No reaction took place at −78 °C, but the starting material was fully consumed when the reaction mixture was allowed to warm up to 0 °C. In the crude reaction mixture two main compounds could be identified. The major component (**12**) has a doublet in the ^1H NMR spectroscopy at δ 4.65 (2 H, J = 48 Hz) and two singlets at δ 3.4 and 2.0 (3 H each). The minor derivative showed a triplet at δ 6.2 (1 H, J = 55 Hz) and two singlets at δ 3.47 and 2.1 (3 H each). After chromatography using 1% EtOAc in petroleum ether as eluent the less polar major compound was changed into the known **13**[11] in 44% overall yield: IR 1730 cm^{-1}; NMR δ 4.78 (2 H, d, J = 48 Hz), 2.52 (2 H, td, J_1 = 7 Hz, J_2 = 2.0 Hz), 1.6–1.07 (8 H, m) 0.88 (3 H, t, J = 7 Hz); ^{19}F NMR −228.27 ppm (t, J = 48 Hz); MS, m/e 146 (M^+), 113 [$(M - CH_2F)^+$], 85 [$(M - COCH_2F)^+$], 61 [$(COCH_2F)^+$]. The more polar derivative, which was unchanged by chromatography, was identified as the difluoro compound **14** isolated in 28% yield: IR 1750 cm^{-1}; NMR δ 6.20 (1 H, t, J = 55 Hz), 3.47 (3 H, s), 2.1 (3 H, s), 1.97 (2 H, t, J = 8 Hz), 1.6–1.0 (8 H, m) 0.88 (3 H, t, J = 7 Hz); ^{19}F NMR −131.85 (1 F, d, J = 55 Hz), −131.62 ppm (1 F, d, J = 55 Hz); MS, m/e 238 (M^+), 179 [$(M - OAc)^+$], 153 [$(C(OMe)(OAC)CHF_2)^+$]. Anal. Calcd for $C_{11}H_{20}F_2O_3$: C, 55.46; H, 8.40. Found: C, 55.73; H, 8.52.

Acknowledgment. We thank the Fund for Basic Research administrated by the Israel Academy of Science and Humanities for supporting this research.

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Stereoelectronic Control in the Photolytic Cleavage of α-Chloro Ketones[1]

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Received December 8, 1986

The UV spectral perturbations created by a chlorine which is axial and α to a ketone have been known for some time[2] and have been attributed, in part, to a mixing of carbonyl π^* and C–Cl σ^* MO's to generate a new, lower-energy LUMO which is ($\pi^* + \sigma^*$).[3] Likewise, the facile

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