8.3 Hz, 1 H), 6.93 (m, 2 H), 6.50 (d, J = 16.2 Hz, 1 H), 6.04 (dd, J = 16.2, 7.6 Hz, 1 H), 3.93 (s, 3 H), 3.64 (s, 3 H), 3.59 (dd, J = 7.6, 5.1 Hz, 1 H), 3.31 (s, 3 H), 2.53 (dd, J = 15.3, 5.7 Hz, 1 H), 2.30 (m, 1 H), 2.16 (dd, J = 15.3, 8.3 Hz, 1 H), 1.01 (d, J = 7.0 Hz, 3 H): ^{13}C NMR (125.8 MHz) 173.4, 154.9, 136.4, 132.3, 130.1, 128.6, 121.7, 119.5, 109.7, 85.4, 56.8, 56.0, 51.5, 37.4, 35.1, 15.6. Anal. Calcd for $C_{16}H_{21}ClO_4$: C, 61.44; H, 6.78. Found: C, 61.38; H, 6.64.

(±)-Oudemansin B (2). To a solution of **24** (38 mg, 0.12 mmol) in THF (2 mL) at −78 °C was added LDA (2.0 mL, 0.13 M). After 5 min a solution of *N*-formylimidazole (0.75 mL, 0.53 M in THF, 0.40 mmol) was added to the orange reaction mixture. The orange color immediately dissipated. The reaction was allowed to warm to ambient temperature over 35 min. The reaction was partitioned between 5% HCl (3 mL) and ether (5 mL). The aqueous fraction was extracted with 5 mL of ether and the combined organic fractions were dried with $MgSO_4$ and concentrated in vacuo. The residue was combined with K_2CO_3 (30 mg, 0.22 mmol) and dimethyl sulfate (0.125 mL, 1.32 mmol) in 4 mL of acetone. After 12 h the reaction was diluted with ether (5 mL), washed with water (5 mL), dried ($MgSO_4$), and concentrated in vacuo. The residue was chromatographed on silica gel (15:1 hexane/ethyl acetate) to yield (±)-oudemansin B (19 mg, 44%) as a clear oil, in addition to recovered **24** (5 mg). **2**: IR (neat oil) 1700, 1640, 1080 cm^{-1}; ^{1}H NMR (500 MHz) δ 7.26 (m, 1 H), 7.20 (s, 1 H), 6.86 (m, 2 H), 6.35 (d, J = 15.9 Hz, 1 H), 5.91 (dd, J = 15.9, 8.5 Hz, 1 H), 3.93 (dd, J = 9.5, 8.5 Hz, 1 H), 3.90 (s, 3 H), 3.77 (s, 3 H), 3.64 (s, 3 H), 3.32 (s, 3 H), 2.99 (dq, J = 9.5, 6.9 Hz, 1 H), 1.26 (d, J = 6.9 Hz, 3 H); ^{13}C NMR (125.8 MHz) δ 168.1, 159.5, 154.8, 136.9, 131.5, 130.4, 130.0, 121.3, 119.4, 112.1, 109.8, 84.8, 61.4, 56.7, 56.0, 51.0, 35.6, 15.7.

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Selective Monofluorination of β-Diketones

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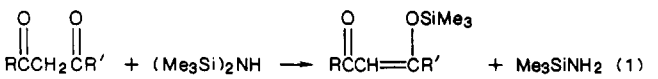
Treatment of silyl enol ethers of β-diketones with 5% F_2 in N_2 results in the formation of 2-fluoro 1,3-diketones. The acyclic derivatives exist as keto tautomers, while the dimedone derivative is enolic. Similarly, the silyl enol ethers of β-keto esters give rise to α-fluoro-β-keto esters.

There have been few attempts to prepare 2-fluoro 1,3-diketones. In special cases, 5-fluoro-5-alkylbarbituric acids can be formed from monofluoromalonates.[1,2] It has also been noted that *trans*-perfluoro-2-pentene can be converted to a 2-fluoro 1,3-diketone.[3] Acid hydrolysis of fluorinated enones has also been shown to give rise to these monofluoro diketones.[4] The lamellar compound, $C_{19}XeF_6$, formed when XeF_6 is absorbed on graphite, reacts with β-diketones to give 40–60% yields of the monofluoro derivatives.[5]

Difluorination can be a complicating factor; for example, the action of xenon difluoride on β-diketones resulted mainly in 2,2-difluoro-1,3-diketones.[6] The monofluoro derivatives could be isolated in low yields when the reaction was performed in dilute solutions with a large substrate to reagent ratio. Similarly, perchloryl fluoride reacted with 2,4-pentanedione in the presence of alkoxide to give the difluoro adduct in 77% yield.[2] However, monofluorination was observed under similar conditions for 2-acylcycloalkanones, cyclic β-keto esters, and diketones.[7] Many of these reactions were complicated by subsequent ring opening. Lerman and Rozen[8] were able to monofluorinate β-keto esters with acetyl hypofluorite, but they did not study β-diketones.

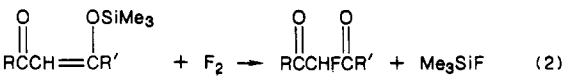
Results

Since the reagents used for fluorination of β-diketones are either expensive or explosive, investigation of the use of dilute fluorine was undertaken. Recently, we have found that trimethylsilyl enol ethers can be selectively fluorinated to give α-fluoro ketones using dilute fluorine.[9] Since trimethylsilyl enol ethers of β-diketones are readily formed[10] as indicated in eq 1, their fluorination was



a, R = R′ = Ph; **b**, R = Me; R′ = Ph; **c**, R = R′ = *t*-Bu; **d**, R = R′ = *n*-Pr; **e**, R = Et; R′ = *n*-Bu

studied. Treatment of these silyl enol ethers with 5% F_2 in N_2 at −78 °C in $CFCl_3$ results in the monofluoro diketone in 26–53% yield (eq 2). Table I summarizes the results and indicates the scope of the reaction. Although the yields are not spectacular, the method does provide only the monofluorinated derivatives and constitutes the only general pathway now available to these compounds.



In our earlier study of α-fluoro ketones,[9] di- and trifluorination of methyl ketones was observed. Thus, not surprisingly, the fluorination of 2-(trimethylsiloxy)-2-penten-4-one (R = R′ = CH_3) resulted in an inseparable complex mixture containing at least five compounds, as

(1) Ishikawa, N.; Takaota, A. *Chem. Lett.* **1981**, 107.
(2) Inman, C. E.; Oesterling, R. E.; Tyczkowski, E. A. *J. Am. Chem. Soc.* **1958**, *80*, 6533.
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(4) Tellier, F.; Sauvetre, R.; Normant, J.-F. *Tetrahedron Lett.* **1986**, *27*, 3147.
(5) Yemul, S. S.; Kagan, H. B.; Setton, R. *Tetrahedron Lett.* **1980**, *21*, 277.
(6) (a) Zajc, B.; Zupan, M. *J. Org. Chem.* **1982**, *47*, 573. (b) Supplementary data.
(7) Machleidt, H.; Hartmann, V. *Justus Liebigs Ann. Chem.* **1964**, *679*, 9.
(8) Lerman, O.; Rozen, S. *J. Org. Chem.* **1983**, *48*, 724.
(9) Purrington, S. T.; Lazaridis, N. V.; Bumgardner, C. L. *Tetrahedron Lett.* **1986**, *27*, 2715.
(10) Chu, D. T. W.; Huckin, S. M. *Can. J. Chem.* **1980**, *58*, 138.

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Table I. Fluorination Products

compd	time (h)	yield, %	bp, °C/torr [mp, °C]	^{19}F NMR	^{1}H NMR	IR ν (C=O) cm^{-1}
3a	1.75–2.5	34	[74–76]	−187 d J_{HF} = 52.2 Hz	6.37 (d, 1 H, J_{HF} = 52.2 Hz), 7.4–7.6 (m, 6 H), 8–8.2 (m, 4 H)	1705
3b	2	23	96/0.5	−189 d J_{HF} = 51 Hz	2.3 (s, 3 H), 6.0 (d, 1 H, J_{HF} = 51 Hz), 7.3–8.2 (m, 5 H)	1700
3c	3	40	67/1.4	−186 d J_{HF} = 50 Hz	1.1 (s, 18 H), 5.6 (d, 1 H, J_{HF} = 49.5 Hz)	1730
3d[a,b]	3	41	72–73/0.5	−195 dm J_{HF} = 51 Hz	0.95 (m, 6 H), 1.65 (m, 4 H), 2.55 (m, 4 H), 5.05 (d, 1 H, J_{HF} = 51 Hz)	1720
3e[a,c]	3	44	77–79/0.6	−195 dm J_{HF} = 51 Hz	0.9 (t, 6 H), 1.4 (m, 4 H), 2.3 (m, 4 H), 4.9 (d, 1 H, J_{HF} = 51 Hz)	1720
4	3.5	42	[149–150]	−171 (s)	1.1 (s, 6 H)8 2.33 (s, 2 H), 2.39 (s, 2 H)	1640
6	2.5	53	81/0.3	−164 (t) J_{HF} = 21 Hz	1.1–1.6 (t, 3 H), 2.1–2.6 (m, 4 H), 3.0–3.3 (t, 2 H), 4.0–4.4 (q, 2 H)	1730–1780
8	2.5	48	52–55/3	−194 dm J_{HF} = 50 Hz	1.1 (t, 3 H), 2.1 (d, 3 H), 4.1 (q, 2 H), 5.0 (d, 1 H, J_{HF} = 49.8 Hz)	1720–1770

[a] Satisfactory analyses not obtained due to decomposition of these compounds. [b] Mass spectral peaks, m/z (relative intensity): 43 (63); 71 (100); 103 (1.1); 131 (7.6); M^+ 174 (1.6). [c] Mass spectral peaks, m/z (relative intensity): 57 (100); 85 (33); 117 (8.6); 145 (2.9); M^+ 174 (1.1).

shown by ^{19}F NMR and GC. Short reaction times were required to prevent overreaction as well as to avoid ring fluorination of the aromatic compounds.

The structure of the resulting 2-fluoro 1,3-diketones is of particular interest. One might expect these compounds to be highly enolized because of the electronegativity of fluorine. Further, while studying monofluoropropenes, Dolbier has found that a single fluorine is thermodynamically more stable at sp^2 carbon than at sp^3 carbon.[11]

The paucity of data in the literature does little to clarify the situation. Yemul, Kagan, and Setton[5] portray the monofluoro adduct of 1,3-diphenyl-1,3-propanedione in the enolic form and state that the structure was deduced from ^{1}H and ^{19}F NMR spectral data that were not given. Similarly, Tellier, Sauvetre, and Normant[4] say that 5-fluoro-3,8-dimethyl-4,6-decanedione (R = $CH(CH_3)CH_2CH_3$, R′ = $CH_2CH(CH_3)CH_2CH_3$) exists in tautomeric equilibrium without supporting spectral data. 1,1,1,3,5,5,5-Heptafluoro-2,4-pentanedione (R = R′ = CF_3) is reported to exist in tautomeric equilibrium with 72% in the keto form.[3] Zajc and Zupan[6b] report that 3-fluoro-2,4-pentanedione shows a fluorine resonance at −198.2 ppm that is a doublet of multiplets with J = 49.5 Hz. In the proton NMR spectrum the 3-proton absorbs at 5.26 ppm with complementary coupling, J = 49.5 Hz. The methyl groups appear at 2.25 ppm as a multiplet, indicative of long range splitting. These data are in accord with the pure keto tautomer.

The results obtained in our study do clarify the situation. The acyclic α-fluoro β-diketones provide the keto tautomers as determined by ^{19}F and ^{1}H NMR. For example, compound **3c** shows only a doublet of 5.6 ppm in the ^{1}H NMR and at −186 ppm in the ^{19}F NMR when first formed. Attempts to tautomerize **3c** by treatment with *p*-toluenesulfonic acid were unsuccessful. However, after 2 months a singlet at −169 ppm is observed in the ^{19}F NMR spectrum corresponding to a decomposition product and no hydroxyl is observed in the infrared spectrum. Compounds **3d** and **3e** decomposed more rapidly. These compounds can enolize in the direction away from the fluorine-bearing carbon and their disappearance may result from condensation reactions. The central acidic C-5 proton of 5-fluoro-4,6-nonanedione (**3d**, R = R′ = *n*-Pr) exchanges rapidly with deuterium in basic D_2O. The doublet at 5.05 ppm in the ^{1}H NMR spectrum disappears while the doublet at −195 ppm in the ^{19}F NMR spectrum collapses to an apparent singlet at −196 ppm. On expansion of the spectrum, a group of three equal peaks is observed with J_{D-F} = 9 Hz. This signal is attributed to the deuteriated diketo tautomer. The pK_a of **3a** was measured and found to be 2 units less than that of the unfluorinated diketone in absolute ethanol.

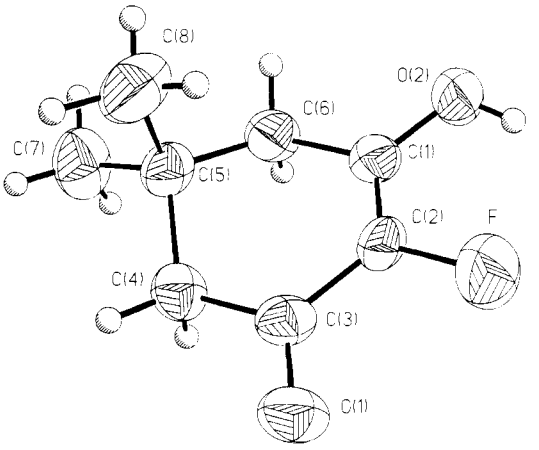
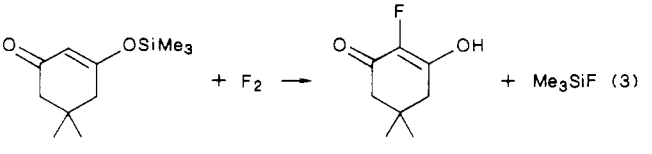


Figure 1. View of the molecule showing thermal ellipsoids with 50% probability for non-hydrogen atoms. Hydrogen atoms are shown as partially hatched circles of arbitrary size.

Interestingly, the fluoro derivatives of cyclic ketones 1,3-cyclohexanedione and dimedone exist in the enolic form as determined by NMR spectroscopy and X-ray crystallography. The ORTEP drawing of 2-fluoro-3-hydroxy-5,5-dimethyl-2-cyclohexenone, **4**, is shown in Figure 1. Like dimedone,[12] the fluorinated derivative crystallizes in the enol form which is hydrogen bonded to two other molecules in a helical manner. The hydrogen bond length for dimedone is 2.593 Å,[12] while that for the fluorinated dimedone is 2.647 Å. Although the fluorine can act as a proton acceptor in a bifurcated bond, OH···O interactions are stronger.[13] Hence, there is no compelling

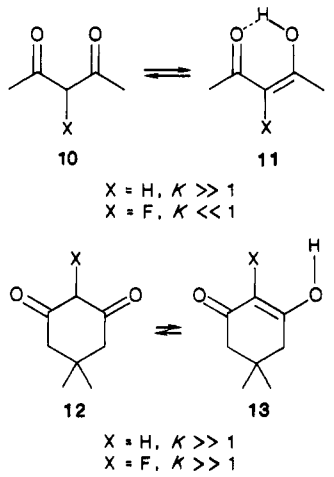


4

(11) Dolbier, W. R., Jr.; Medinger, K. S.; Greenberg, A.; Liebman, J. R. *Tetrahedron* **1982**, *38*, 2415.

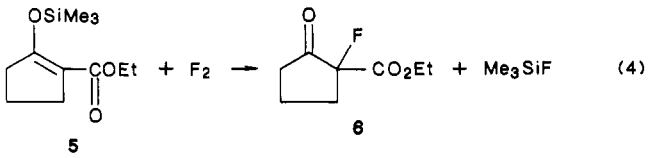
(12) Semmingsen, D. *Acta Chem. Scand., Ser. B.* **1974**, *28*, 169.

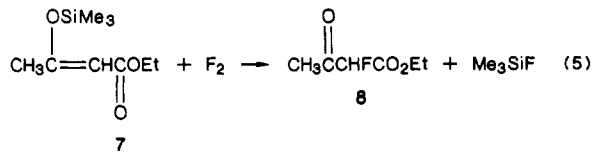
Chart I



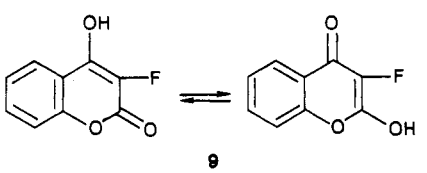
evidence for hydrogen bonding to fluorine. The crystal data and packing diagram are available as supplementary data.

In order to further extend the scope of the reaction, the silyl enol ethers of ethyl acetoacetate and ethyl 2-oxocyclopentanecarboxylate were prepared and fluorinated (eq 4 and 5). Thus, α-fluoro-β-keto esters can also be synthesized through their silyl enol ethers.





Although Burdett and Rogers[14] determined that ethyl α-fluoroacetoacetate exists 15% in the enol form, the results obtained here and the observations of Lerman and Rozen[8] clearly indicate that it is purely the keto tautomer. The cyclic 3-fluoro-4-hydroxycoumarin, **9**,[15] and fluorinated β-keto-δ-butyrolactones exist in the enolic form. Kitazume attributes the enolic structure to the presence of intramolecular hydrogen bonding.[16]

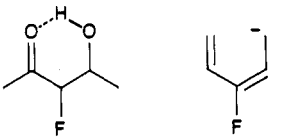


9

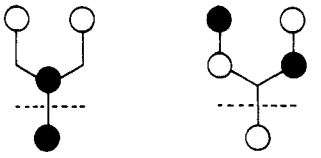
Discussion

Examination of the keto–enol content of the products from fluorination of 1,3-diketones reveals an arresting dichotomy—the fluorinated acyclic cases prefer the diketo form whereas the fluorinated cyclic case favors the enolic tautomer. This difference is underscored by the fact that the hydrogen analogues, both cyclic and acyclic, generally show a strong preference for the enolic form.[14] These relations are summarized in Chart I.

The exceptional member of this series appears to be **10**, X = F. The question then arises: does F stabilize the diketone **10** or destabilize the enol **11**? A simple explanation in terms of the relative stability of a single F attached to sp^3 carbon (**10**) vs. an sp^2 carbon (**11**) does not lead to the correct answer, for Dolbier[11] has found that $FC(H)=CHCH_3$ is more stable than $CH_2=CHCH_2F$. We note in our cases, however, that in **11**, F is not just attached to an ethylenic group, but a more extended conjugated framework which is isoelectronic with a pentadienyl anion moiety.



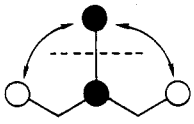
To estimate the electronic effects of such an arrangement, we combine[17] the HOMO of a pentadienyl anion system with a filled p orbital on F, structure **14**. This



14 **15**

HOMO–HOMO interaction is destabilizing in terms of primary orbital overlap. Combining the LUMO of a pentadienyl anion with a filled F p orbital, structure **15**, does not provide any stabilizing effect for there is a node[18] on the central carbon to which F is bound. Thus, we conclude that F destabilizes **11** with respect to **10**, leading to $K < 1$.[3]

If F destabilization of the enol form accounts for the behavior of **10** and **11**, then why does the fluorinated cyclic case (**12** and **13**) follow the norm where the enolic partner is favored with H and F. We note in this instance that the shape of the conjugated framework is necessarily altered to accommodate the ring. Combining a filled p orbital from F with the HOMO of this newly shaped pentadienyl anion system still results in a destabilizing primary HOMO–HOMO interaction, but now *two* secondary orbital interactions indicated by the double-headed arrows in **16** decrease the net overlap and thus negate to a large extent the destabilization. Since F does not appreciably destabilize the enol in this case, the factors which generally favor the enol[19] prevail, making **13** more stable than **12** when X = H and F.

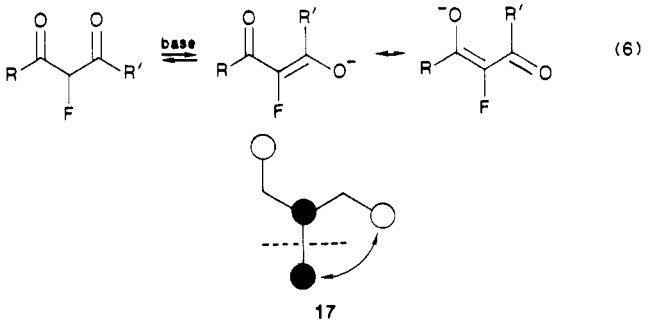


16

Finally, we must account for our observation that **3a** (R = R′ = Ph) is a stronger acid than the nonfluorinated analogue. This fact at first may appear puzzling since our explanation for the position of keto–enol equilibria in acyclic 1,3-diketones pivoted on the fluorine atom destabilizing the enol form. Why then does not fluorine destabilize the *enolate* as well and make the fluorinated

(13) Christe, K. O. *J. Fluorine Chem.* **1987**, *35*, 621.
(14) Burdett, J. L.; Rogers, M. T. *J. Am. Chem. Soc.* **1964**, *86*, 2105.
(15) Dmowski, W. *J. Fluorine Chem.* **1982**, *20*, 589.
(16) Kitazume, T. *J. Fluorine Chem.* **1987**, *35*, 287.
(17) Whangbo, M.-H.; Wolfe, S. *Israel J. Chem.* **1980**, *20*, 36.
(18) This will be strictly true only for the pentadienyl anion which is used to simulate the conjugated enol. In any case, the coefficient at the middle carbon atom should be ≃0.
(19) Schwarzenbach, G.; Suter, H.; Lutz, K. *Helv. Chim. Acta* **1940**, *23*, 1191.

diketone less acidic than the nonfluorinated species? The reason, we believe, is to be found in eq 6, which shows that



(6)

the enolate derived from **3** does not have the same conformation[20] as the hydrogen-bonded enol depicted in **11**. On the basis of this trend our orbital picture for the enolate in eq 6 would be described in **17**. In this geometry not only are the two partially charged oxygen atoms remote from each other but also the destabilizing HOMO–HOMO interaction of fluorine with the pentadienyl anion framework is muted by the secondary orbital interaction shown by the double-headed arrow in **17**. These factors, combined with the inductive effect of fluorine, serve to favor enolate formation in **3a** and make the fluorinated diketone more acidic than the nonfluorinated diketone.[21]

We conclude, therefore, that the effect of F on the keto–enol equilibrium and acidity depends on the shape of the conjugating framework to which the fluorine is attached. Additional experimental tests of these ideas are under study.

Experimental Section

Melting points were determined on a Thomas-Hoover melting point apparatus and are uncorrected. ^{1}H NMR (90 MHz) and ^{19}F NMR (84.67 MHz) spectra were obtained in $CDCl_3$ and recorded on a Varian FM-390 spectrometer. Chemical shifts are reported in ppm downfield from internal tetramethylsilane and external $CFCl_3$. Infrared spectra were obtained on a Beckman-Acculab-1 spectrometer. Microanalyses were performed by Atlantic Microlab, Inc., Atlanta, GA. The 5% F_2 in N_2 was supplied by Air Products and the keto derivatives were available from Aldrich. The mass spectra were obtained on a Hewlett-Packard 5985B-TRE6, with direct insertion probe (temperature program 50 °C-300 °C at 20°/min); EI 70 eV.

Preparation of Silyl Derivatives. The silyl enol ethers were prepared according to the procedure of Chu and Huckin.[10] **2a**: 92%, hydrolyzes rapidly; ^{1}H NMR 0.15 (s, 9 H), 6.75 (s, 1 H), 7.10–7.85 (m, 10 H). **2b**: 79%; bp 118–122 °C/0.7 mmHg (lit.[22] bp 110–111 °C/0.2 mmHg); ^{1}H NMR 0.2 (s, 9 H), 2.1–2.2 (2s, 3 H), 5.9–6.2 (m, 1 H), 7.2–7.8 (m, 5 H). **2c**: 82%; bp 74 °C/1.1 mmHg (lit.[23] bp 44–45 °C/0.04 mmHg); ^{1}H NMR 0.1 (s, 9 H), 1.2 (s, 18 H), 5.7 (s, 1 H). **2d**: 62%; 81–83 °C/0.7 mmHg; ^{1}H NMR 0.3 (s, 9 H), 0.9–1.1 (m, 6 H), 1.5–1.8 (m, 4 H), 2.1–2.5 (m, 2 H), 2.6–2.9 (t, 2 H), 5.5 (s, 1 H). **2e**: 66%; 86–90 °C/0.5 mmHg; ^{1}H NMR 0.3 (s, 9 H) 0.8–1.6 (m, 8 H), 2.1–2.3 (t, 4 H), 5.4 (s, 1 H). 5,5-Dimethyl-3-[(trimethylsilyl)oxy]-2-cyclohexen-1-one: mp 56–57 °C (lit.[10] mp 56–58 °C); ^{1}H NMR 0.3 (s, 9 H), 1.1 (s, 6 H) 2.18 (s, 2 H), 2.21 (s, 2 H), 5.4 (s, 1 H). **5**: 75%; bp 106 °C/0.9 mmHg; ^{1}H NMR 0.4 (s, 9 H), 1.7 (t, 3 H), 2.3–2.5 (m, 4 H), 3.55 (t, 2 H), 4.58 (q, 2 H). **7**: 99%; bp 95–97 °C/18 mmHg (lit.[24] bp 76–79 °C/7 mmHg); ^{1}H NMR 0.2 (s, 9 H), 1.2 (t, 3 H), 2.2 (s, 3 H), 4.0 (q, 2 H), 4.95 (s, 1 H).

Fluorinations. The diluted F_2 was passed through solid NaF and into a gas trap containing 0.005–0.01 mol of the silyl derivative in 30 mL of $FCCl_3$ at −78 °C. The exit gases were vented through two iodide traps in order to decompose any unreacted fluorine. The solvent was removed under reduced pressure and the product was distilled. The fluorination times, percent yield, boiling or melting point, and ^{1}H and ^{19}F NMR data are given in Table I. Compounds **3a** and **3c** showed no OH in the infrared spectrum while the fluorodimedone showed absorbance at 3100–3500 cm^{-1}.

X-ray Data Collection and Structure Determination. Colorless, large, plate-like crystals of fluorodimedone, **4**, were grown from a saturated acetone solution by slow evaporation at room temperature. Unit cell parameters were derived from a least-squares refinement of the setting angles of 25 reflections with $45° \leq 2\theta \leq 65°$. The intensity data were corrected for background and Lorentz and polarization effects. Absorption corrections were not needed. The structure was solved by direct methods and refined by the blocked-cascade least-squares refinement technique to an R factor of 0.051. The quantity minimized was $\Sigma w(\Delta F)^2$. Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were located from a difference Fourier and were refined with isotropic thermal parameters. X-ray atomic scattering factors were taken from the International Tables.[25]

X-ray data were collected on a Nicolet R3m/μ (Syntex $P\bar{1}$ upgraded) automated four-circle diffractometer. All calculations were performed on a Data General microeclipse desktop computer with the crystallographic program package SHELXTL.[26] Crystal data and other crystallographic parameters as well as tables of fractional atomic coordinates, bond distances and angles, thermal parameters, and observed and calculated structure amplitudes are available as supplementary material.

pK_a Determinations. The pK_a's of **1a** and **3a** were determined by titration with 0.05 M NaOH in absolute ethanol. The titrations of the diketones (0.24 g in 40 mL absolute ethanol) were monitored with a Fisher Accumet Model 220 pH meter and a standard glass electrode. After plotting pH values vs. the volume of titrant, the pH was extrapolated from half the volume of titrant required for neutralization. **1a**, pH 10.7; **3a**, pH 8.5.

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Registry No. **1a**, 120-46-7; **1b**, 93-91-4; **1c**, 1118-71-4; **1d**, 14090-88-1; **1e**, 95050-78-5; **2a**, 73845-27-9; **2b**, 38109-75-0; **2c**, 109801-20-9; **2d**, 109801-22-1; **2e**, 109801-23-2; **3a**, 109801-24-3; **3b**, 109801-25-4; **3c**, 109801-26-5; **3d**, 109801-27-6; **3e**, 109801-28-7; **4**, 109801-21-0; **5**, 17962-60-6; **6**, 84131-44-2; **7**, 13257-83-5; **8**, 1522-41-4; 5,5-dimethyl-3-[(trimethylsilyl)oxy]-2-cyclohexen-1-one, 10416-78-1; dimedone, 126-81-8; ethyl 1-oxocyclopentane-2-carboxylate, 611-10-9; acetoacetate, 541-50-4.

Supplementary Material Available: Summary of crystal parameters, tables of atomic coordinates, thermal parameters, bond lengths, and bond angles, and a packing diagram for **4** (4 pages). Ordering information is given on any current masthead page.

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